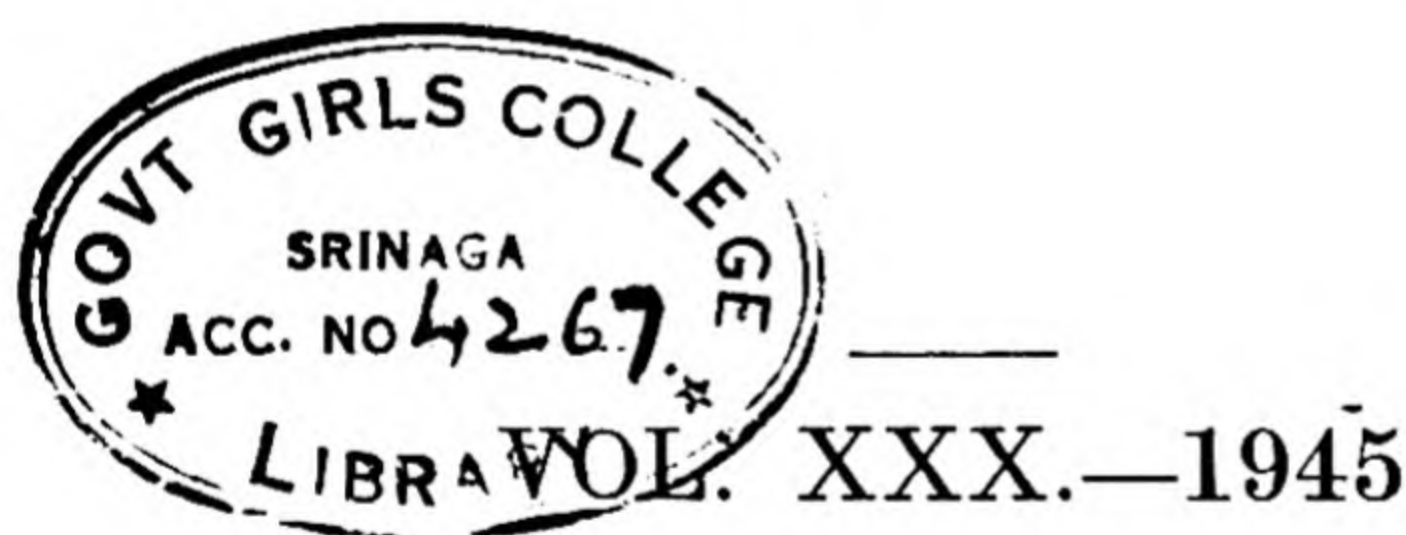


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# REPORTS

OF THE

## PROGRESS OF APPLIED CHEMISTRY

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### CHEMICAL ENGINEERING, PLANT, AND MACHINERY.

BY F. RUMFORD, PH.D., B.Sc., F.R.I.C., M.I.CHEM.E.,  
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DURING the period under review, hostilities terminated abruptly in the second great war of modern times with a startling demonstration of scientific development. The production of atomic energy, or rather nuclear energy, on a large scale opens up enormous possibilities in all fields, and not least in the realm of the design of chemical plant. It was, in fact, a great achievement in chemical engineering to translate on to a gigantic scale processes that had hitherto been practiced only in a special laboratory. In the pamphlets<sup>1</sup> published by the British and United States Governments, some description is given of the preliminary stages of this translation, although, of course, the final stages are still a State secret. It will clearly be necessary, in the near future, to develop large-scale plant for the separation of isotopes, and to handle very large quantities of radioactive substances.

At the same time, as long as effective disintegration is confined to naturally radioactive elements, a rapid extension in the application of flotation and other ore-concentrating processes may be expected. The very valuable nature of the concentrate will allow complicated and exhaustive working. It may be noted that a paper by E. F. McTaggart,<sup>2</sup> in the 1942 *Transactions of the Institution of Chemical Engineers*, recently published, covers the preliminary stages of such a separation.

While it is too soon to expect any relaxation of control on publication of accounts of plant development made during the war, it is clear that there will be in this country at the moment a large amount of surplus chemical plant, especially in the fields of sulphuric and nitric acid manufacture.<sup>3</sup> It will be a matter of some difficulty to decide whether these plants should be scrapped or set to work on peace-time projects. The surplus capacity which also exists in synthetic ammonia plants may be combined with that of the acid plants in a greatly increased production of artificial fertilisers with little modification of plant, but it is doubtful whether such an arrangement could compete economically with standard plant built in better localities. The existence, then, of large, more or

<sup>1</sup> "Atomic Energy" and "Statement Relating to the Atomic Bomb."  
<sup>2</sup> *Trans. Inst. Chem. Eng.*, 1942, 20, 65; cf. B., 1942, I, 462.  
<sup>3</sup> *Chem. and Ind.*, 1945, 242.



less idle chemical plants offers a challenge to chemical technologists which must be met rapidly, or the plant will undoubtedly be scrapped.

An interesting addition<sup>4</sup> to the periodicals dealing with chemical engineering is the *Journal of the Chemical Engineering Society of the Imperial College*, London. It may be noted here that the School of Chemical Engineering at the Imperial College was the only one of the three London schools to escape serious damage, and was thus enabled to keep at work throughout the war.

### FLUID FLOW.

The rate of flow of liquids through fine channels in hard materials tends to fall off slowly from a relatively high initial value, according to C. K. Wentworth<sup>5</sup>; he suggests that this phenomenon is due to the gradual building up of static adsorbed films, and that it is confined to such liquids as wet the solid surface readily. N. C. Sen Gupta<sup>6</sup> has found that certain oil-well sands show abnormal changes in air-permeability as the water content increases; values remain constant until a certain critical content is reached, and then decrease rapidly. Other types of sand show, as might be expected, a steady fall in permeability with increasing water content. G. L. Hassler and E. Brunner<sup>7</sup> have described a centrifugal technique for the determination of capillary pressures in porous materials. The sample of saturated material, in a suitable container, is spun in a centrifugal device at steadily increasing speed; the volume of expelled liquid is read by means of a stroboscope, without interrupting the centrifugal motion.

R. C. Martinelli<sup>8</sup> and his co-workers have studied the flow forms of gas and liquid mixtures in circular pipes; they used mixtures of air with several different liquids, and by the use of glass tubes were enabled to make photographic studies of flow. General formulæ for pressure drop were constructed and their application to boiling liquids, as in water-tube boilers, was discussed. The work of S. I. Kosterin<sup>9</sup> appears to follow similar lines, but only water-air mixtures were used; here the variations in pressure drop with a modified Reynolds criterion were measured, and some attention was given to the transmission of pulsations in pressure.

G. A. Davis<sup>10</sup> has described means of securing uniform flow of hot gases from a main flue into regenerators, and given some account of the mode of flow of hot gases in heating flues; he puts forward suggestions for decreasing the pressure drop in such installations. The stack gases

<sup>4</sup> *J. Imperial Coll. Chem. Eng. Soc.*, 1945, 1.

<sup>5</sup> *Amer. J. Sci.*, 1944, 242, 478; B., 1945, I, 3.

<sup>6</sup> *Indian J. Physics*, 1943, 17, 338; B., 1945, I, 2.

<sup>7</sup> *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1817; B., 1945, I, 203.

<sup>8</sup> R. C. Martinelli, L. M. H. Boelter, T. H. M. Taylor, E. G. Thomson, and E. H. Morrin, *Trans. Amer. Soc. Mech. Eng.*, 1944, 66, 139; B., 1944, I, 347.

<sup>9</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1943, No. 11/12, 37; B., 1945, I, 2.

<sup>10</sup> *Blast Furn. and Steel Plant*, 1945, 33, 568.



leaving these large industrial furnaces are frequently a source of local nuisance, and the way in which these effluents are diluted by air at the top of a stack may be very important. G. E. McElroy, C. E. Brown, L. B. Berger, and H. H. Shrenk<sup>11</sup> have built up a scale model for a study of this dilution; they show, by means of photographic devices, the jet of warm gas gradually bending down until its axis coincides with the wind direction, but they were unable to derive any simple rule for dilution effects. A. Kolin<sup>12</sup> has devised a method of measuring fluid flow which should be especially suitable for exploring velocity distribution in pipes. The conduit is electrically insulated, and a magnetic field at right angles then produces an e.m.f. between two fine filaments immersed in the fluid.

The design of sprays for chemicals has not been very fully investigated except for certain special purposes such as spray drying, and an account<sup>13</sup> of sprays for sodium carbonate solutions, designed to give a specific droplet size and spray shape, may be of general interest. The sprays, described by S. M. Doble, were for covering coke with an activating layer of alkali. It has long been an observed fact that the smaller particles in a solid-liquid slurry facilitate the suspension of larger fragments, and this has now been made the basis of a patent<sup>14</sup> for the pumping of slurries.

Most technologists will have experienced difficulty due to valve blockage when connecting control systems to a single valve in which inlet and outlet pressures remain approximately constant, whatever the rate of flow. By the use of two valves,<sup>15</sup> with a short intermediate conduit, this difficulty may be overcome, as the state of the valve passages is reflected in the intermediate pressure of the conduit.

#### HEAT TRANSFER.

A. L. Waddams,<sup>16</sup> continuing his work (cf. *Ann. Repts.*, 1944, 29, 8) on the flow of heat through beds of granular solid materials, finds that in general the conductivity increases with size of individual particle. This is held to be due to increases in convective disturbance in the void spaces, although surface conditions at the point of contact can affect results. O. A. Tschuchanova and E. A. Schapatina<sup>17</sup> have been carrying out similar work in Russia, using piles of regularly shaped fragments (copper cylinders and steel balls). Z. F. Tschuchanov<sup>18</sup> has measured heat transfer in a burning fuel bed, and notes that heat flow increases with a decrease in the particle size of the fuel; here, however, in contrast to the work of Waddams, heat transfer is primarily by radiation.

<sup>11</sup> *U.S. Bur. Mines*, 1944, *Tech. Paper* 657; B., 1945, I, 3.

<sup>12</sup> *Ind. Heating Eng.*, 1945, 7, 158.

<sup>13</sup> *Engineering*, 1945, 159, 21, 61, 103.

<sup>14</sup> B.P. 567,079; B., 1945, I, 141.

<sup>15</sup> B.P. 569,943; B., 1945, I, 317.

<sup>16</sup> *J.S.C.I.*, 1944, 63, 337; B., 1945, I, 49.

<sup>17</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1943, No. 7, 62.

<sup>18</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, 44, 269; B., 1945, I, 175.



R. A. Soban and A. L. London<sup>19</sup> report experimental confirmation of their mathematical expressions for the rate of freezing of water shapes, and have extended the work to the freezing of typical root vegetables. P. Drossbach<sup>20</sup> has discussed the mechanism of heat transfer in reaction systems where the velocity of reaction varies with temperature. He gives as a typical case the interaction of alumina, silica, and carbon in an electric furnace.

Z. F. Tschuchanov,<sup>21</sup> in a study of heat flow through fluid films, suggests that transfer between films moving at different velocities is by molecular velocity pulsations; in extension of this he derives an expression for the Nusselt number of the system which gives good agreement with experimental values. The special case in which gases flow through a tube of constant cross-section with velocities approximating to that of sound has been analysed by B. Szczeniowski<sup>22</sup>; he suggests that heat transfer by convection cannot increase indefinitely with velocity, as with velocity equal to that of sound, heat flow would cease. A maximum value for heat transfer must, therefore, be reached at velocities considerably above this figure. Values for very high rates of heat transfer will probably become important in the generation of atomic power, owing to the very small area of the disintegrating solid masses. These have been,<sup>23</sup> in the past, uranium "slugs" in sealed aluminium cans, and future developments are difficult to foresee. It is obvious, however, that very large amounts of energy will require to be taken up from relatively tiny surfaces, with the added complication of intense radioactivity. It is hoped that further details of heat transfer in the "atomic" plants will soon be available.

This problem may increase interest in the special heat-transfer fluids, of which P. W. Parsons and B. J. Gaffney<sup>24</sup> have presented an analysis on the basis of film coefficients obtainable for a given pressure drop per unit of heat-transfer surface. A recent example of these fluids<sup>25</sup> is a mixture of dichlorobenzene and cyclohexanol. A special case of heat flow<sup>26</sup> through films at high temperatures is met with in the flow of coal-ash slag on furnace walls. P. Cohen and W. T. Reid, treating the film as a plastic solid, changing at a fixed temperature to a viscous fluid, have derived values for thickness of the slag layer and the rate of heat transfer through the film. T. C. Patton<sup>27</sup> has suggested standard graphical methods for the treatment of unsteady-state heat flow problems.

Much attention has been paid to the problems of high-frequency

<sup>19</sup> *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 39; B., 1945, I, 202.

<sup>20</sup> *Z. Elektrochem.*, 1943, **49**, 316; B., 1944, I, 345.

<sup>21</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **43**, 27; B., 1945, I, 139.

<sup>22</sup> *Canad. J. Res.*, 1945, **23**, A, 1; B., 1945, I, 201.

<sup>23</sup> "Atomic Power," P.88.

<sup>24</sup> *Chem. Met. Eng.*, 1945, **52**, No. 1, 100; B., 1945, I, 169.

<sup>25</sup> U.S.P. 2,314,636; B., 1944, I, 380.

<sup>26</sup> *U.S. Bur. Mines*, 1944, *Tech. Publ.* 663; B., 1945, I, 81.

<sup>27</sup> *Ind. Eng. Chem.*, 1944, **36**, 990; B., 1945, I, 82.



"dielectric" heating. L. Hartshorn<sup>28</sup> shows that the heating is proportional to the field strength, frequency, and the loss factor; costs are high and the overall efficiency is low, but the selective, internally generated heat has advantages which outweigh these factors for most types of laminated material. T. W. Dakin and R. W. Auxier<sup>29</sup> show how the heat generated, determined by the product of the loss factor and the frequency, will in general increase with frequency, but will exhibit peaks characteristic of the material being heated. J. W. Robertson,<sup>30</sup> in the course of a general review, has given some statements of the cost of this system of heating, and R. R. Baker and C. J. Madsen<sup>31</sup> have suggested possible applications in the paper industry, with special reference to thick cardboard sections.

The question of economic thickness of lagging has been reopened by C. B. Bradley, C. E. Ernst, and V. Paschkis.<sup>32</sup> For plant in intermittent operation the mathematical solution is much more involved than in the standard "steady-flow" case, but an electrical analogy is used to derive a series of curves showing heat loss over a wide experimental range; figures for the economic thickness can be obtained from these curves. V. Paschkis and M. P. Heisler<sup>33</sup> have studied the theoretical loss involved when lagging is "short-circuited" by metal strips or bars passing from the hot interior through the lagging to the outer surface. An interesting adaptation<sup>34</sup> of aluminium foil for heat insulation is to mount it on helical coils of wire, which then act as spacers for the insulation.

Practical coefficients of heat transfer have been suggested by E. F. Lype<sup>35</sup> for the case of hot gases flowing over banks of boiler tubes. A patent<sup>36</sup> on tube and shell heat interchangers deals with special baffles, from fins and rows of studs, arranged on the tubes to give relatively high heat transfer with a low pressure drop. A spiral-plate heat interchanger, made up from interwound metal spirals, has recently been described,<sup>37</sup> and would appear to present certain advantages in ease of fabrication. E. G. Peterson<sup>38</sup> has given an account of intensive heating furnaces used in the oil industry, which operate at pressures up to 50 lb. per sq. in. and loadings up to 2,500,000 B.Th.U. per cu. ft. per hr.

### DISTILLATION.

J. A. Storrow<sup>39</sup> has attempted to distinguish between the resistance of the liquid and vapour films to mass transfer in distillation. He

<sup>28</sup> *Chem. and Ind.*, 1944, 322; B., 1945, I, 1.

<sup>29</sup> *Ind. Eng. Chem.*, 1945, 37, 268; B., 1945, I, 169.

<sup>30</sup> *Ibid.*, 1944, 36, 440; B., 1944, I, 345.

<sup>31</sup> *Paper Trade J.*, 1944, 119, *TAPPI Sect.*, 73; B., 1945, I, 81.

<sup>32</sup> *Trans. Amer. Soc. Mech. Eng.*, 1945, 67, 93; B., 1945, I, 202.

<sup>33</sup> *Ibid.*, 1944, 66, 653; B., 1945, I, 201.

<sup>34</sup> B.P. 569,633; B., 1945, I, 315.

<sup>35</sup> *Mech. Eng.*, 1944, 66, 254; B., 1944, I, 377.

<sup>36</sup> B.P. 569,573; B., 1945, I, 315.

<sup>37</sup> B.P. 563,985; B., 1944, I, 380.

<sup>38</sup> *Trans. Amer. Soc. Mech. Eng.*, 1944, 65, 433; B., 1945, I, 273.

<sup>39</sup> *Trans. Inst. Chem. Eng.*, 1945.



used a simple wetted-wall column, for which attempts have previously been made to derive dimensional equations for mass transfer, especially as regards effective thickness of the vapour film; the results, however, did not agree with these equations, while both liquid and vapour films offered appreciable resistance. W. Kuhn and K. Ryffel<sup>40</sup> have attempted the correlation between the essential dimensions of wetted-wall columns and their fractionating efficiency; they find that the efficiency may vary widely with the mixture being separated and with the temperature and pressure of the distillation. R. Edgeworth-Johnstone<sup>41</sup> has followed up his previous work on batch mixtures with the derivation of a general method for determination of the total amount to be vaporised for a given yield of more volatile component from a binary mixture; as before, this is based on the condition of a constant product quality with a varying reflux.

R. E. Treybal<sup>42</sup> has suggested a graphical method for the determination of equilibrium conditions in a ternary mixture, where relative activity coefficients of the components in binary mixtures are known; the method has been applied to several mixtures with results which were in good agreement with experimental results. H. H. Hummel,<sup>43</sup> in a graphical solution of multi-component fractionation, selects a key component and constructs a curve of equilibrium concentration against plate numbers, by calculation from known relative volatilities. The problem has also been discussed from a practical point of view by C. G. Kirkbride.<sup>44</sup>

D. F. Othmer and R. F. Benenati<sup>45</sup> have presented data for the vapour-liquid equilibrium between water and several organic solvents, at sub-atmospheric pressures. R. L. Huntington<sup>46</sup> has discussed the form of vapour-liquid equilibria with two liquids which are to some extent immiscible.

A number of laboratory and small technical columns of high theoretical plate equivalence have been described in literature, but it is not fully realised, according to E. A. Coulson,<sup>47</sup> that such columns develop their full efficiency only slowly; a time lag of several hours at total reflux is necessary for quite small columns, and in such cases a very small vapour leak from the head of the column may exercise a very large influence over the results obtained. J. Griswold, J. W. Morris, and C. F. Van Berg<sup>48</sup> have described some "screen plate" laboratory columns, up to 2 in. in diameter, which might be developed to a larger size; the plates are of wire gauze, and with normal plate efficiencies have a pressure drop

<sup>40</sup> *Helv. Chim. Acta*, 1943, **26**, 1693; B., 1945, I, 50.

<sup>41</sup> *Ind. Eng. Chem.*, 1944, **36**, 1068; B., 1945, I, 83.

<sup>42</sup> *Ibid.*, 875; A., 1945, I, 66.

<sup>43</sup> *Trans. Amer. Inst. Chem. Eng.*, 1944, **40**, 445; B., 1945, I, 50.

<sup>44</sup> *Petrol Refiner*, 1944, **23**, 321.

<sup>45</sup> *Ind. Eng. Chem.*, 1945, **37**, 299; A., 1945, I, 165.

<sup>46</sup> *Petrol Refiner*, 1944, **23**, 351.

<sup>47</sup> *J.S.C.I.*, 1945, **64**, 101; C., 1945, 213.

<sup>48</sup> *Ind. Eng. Chem.*, 1944, **36**, 1119; B., 1945, I, 90.



of 0.3 in. of water gauge per plate. E. Hilberath<sup>49</sup> has published a review of the various types of laboratory column available in Germany.

R. H. Ewell, J. M. Harrison, and L. Berg<sup>50</sup> have discussed the effect of molecular constitution on the ability of liquids to form azeotropes, suggesting that deviations from Raoult's law can be predicted from hydrogen-bonding capacity. In support of this L. Berg and J. M. Harrison,<sup>51</sup> with C. W. Montgomery, have cited the fact that the most efficient azeotrope-formers for dehydrating pyridine are aliphatic ethers. They claim that the relative hydrogen-bond systems of water, pyridine, and the ethers would suggest this result. A patent<sup>52</sup> on azeotropic separation describes the use of two entrainers in series, one of which is highly efficient but difficult to recover, and the other less efficient and easier to recover; thus toluene may be recovered from paraffins by the use of dioxan and methyl alcohol.

Several developments in the design of column plates have appeared recently. E. Kirschbaum<sup>53</sup> has described a "trickling plate" which has the characteristic of a large interfacial area between liquid and vapour; it is, however, very sensitive to load, the liquid hold-up increasing rapidly with vapour velocity. Kirschbaum, with K. Leister,<sup>54</sup> has also described a modified sieve plate, with baffles for reflux flow, which is rather more efficient than ordinary perforated plates. An arrangement<sup>55</sup> of liquid downtakes which ensures parallel liquid flow on each plate has been patented; the pipes are all in the same vertical line, but each alternate pipe is set on a different radius, and baffles of S form ensure that the liquid flows around a full 360 degrees before descending to the next plate. A column<sup>56</sup> has been devised with alternate annular and circular plates, having sloping baffles to direct vapour flow; it is claimed that very high vapour velocities can be attained. Another form<sup>57</sup> of column, reminiscent of scrubbing towers, has a series of chambers in which liquid and vapour flow co-current, while passing in opposite directions at the outlet of each chamber.

In the operation<sup>58</sup> of benzole stills, separation between toluene and benzene can be made more complete by working the column on total reflux, and for shorter intermittent periods, with no reflux, withdrawing also the liquid from the top plate; the method is of general application, wherever exhaustive separation is required. It is claimed<sup>59</sup> that entrainment and irregular working, common while operating with very low

<sup>49</sup> *Oel u. Kohle*, 1943, 39, 875.

<sup>50</sup> *Ind. Eng. Chem.*, 1944, 36, 871; B., 1945, I, 50.

<sup>51</sup> *Ibid.*, 1945, 37, 585; A., 1945, I, 268.

<sup>52</sup> U.S.P. 2,376,870.

<sup>53</sup> *Z. Ver. Deut. Ing. Verfahrenstech.*, 1943, 31, 6.

<sup>54</sup> *Chem. Technik*, 1943, 16, 107; B., 1945, I, 313.

<sup>55</sup> U.S.P. 2,327,993; B., 1945, I, 317.

<sup>56</sup> U.S.P. 2,315,190; B., 1944, I, 382.

<sup>57</sup> B.P. 569,039; B., 1945, I, 280.

<sup>58</sup> B.P. 565,919, 565,921, and 565,945; B., 1945, I, 87.

<sup>59</sup> U.S.P. 2,323,047; B., 1945, I, 173.



reflux ratios, can be improved by the circulation of an additional component in the top plates of the column. The centrifugal principle of rectification continues to attract attention, and patents<sup>60</sup> on modifications of the original rotating spiral continue to appear. A ring packing giving a somewhat reduced pressure drop is described by A. Gotzen,<sup>61</sup> and is of the Raschig type, with perforated walls.

In a discussion on the plant required for vacuum working, H. Griffiths<sup>62</sup> points out that the pumps used must give an end vacuum considerably lower than the working pressure required. For absolute pressures of about 12 cm. Hg, wet vacuum pumps combined with a jet condenser are quite satisfactory, whilst for pressures down to about 1 mm., the reciprocating pump, with pressure equalisation, is perhaps a little better in chemical works than the rotary oil-sealed type. For lower pressures, diffusion pumps, which really originated in work by Gaede, need backing units, and the modern tendency is to design for backing pressures as high as 15 mm. Hg. G. J. Stockman<sup>63</sup> has described a three-stage steam-jet exhaustor system working on the distillation of glycerin at 6 mm. Hg pressure.

#### ABSORPTION AND EXTRACTION.

In an attempt to derive a general equation for absorption rates, E. G. Scheibel and D. F. Othmer<sup>64</sup> put forward a form based on relative fluid velocities and the diffusivity of the solute in both phases; they quote a number of results to show that the variation with fluid velocities is established, but indicate that the diffusion effects are not very clear. In the case of mass transfer between two liquids, using a perforated plate column for contact, R. W. Moulton and J. E. Walkey<sup>65</sup> found that the relative liquid rates had little effect on mass transfer; actual interphase velocities were probably settled in this case by the plate spacing etc. The system used was paraffin-water, with methyl ethyl ketone as the common solute, and plate efficiencies were surprisingly low—about 7% or thereby.

W. C. Peck<sup>66</sup> has suggested a general equation for mass transfer in the extraction of solids, with constants to cover such resistances as the interface reaction, cell wall resistance, and diffusion into the bulk of the extracting liquid. The most important factor in a series of extractions, such as might be carried out in a battery of leaching vessels, would appear to be the degree of separation of concentrated liquid from the residual solid; this separation is dependent on particle size, fluid viscosity, and similar properties. A "theoretical cell" concept can be employed for

<sup>60</sup> U.S.P. 2,182,566; B., 1944, I, 382. U.S.P. 2,317,952; B., 1945, I, 87.

<sup>61</sup> *Chem. Technik*, 1942, 15, 86; B., 1945, I, 137.

<sup>62</sup> *Chem. Tr. J.*, 1945, 117, 464, 485.

<sup>63</sup> *Chem. Met. Eng.*, 1945, 52, No. 4, 100.

<sup>64</sup> *Trans. Amer. Inst. Chem. Eng.*, 1944, 40, 611; B., 1945, I, 170.

<sup>65</sup> *Ibid.*, 695; B., 1945, I, 169.

<sup>66</sup> *Chem. and Ind.*, 1944, 439.



the study of an extraction battery, with a "cell efficiency" on the same basis as plate efficiency in fractional distillation. The complications inherent in this problem are further indicated<sup>67</sup> by J. O. Osburn and D. L. Katz, in a study of the extraction of soya beans. They found that the rates of extraction of oil from these beans (in flakes) corresponded to the presence of capillary channels running through a solid block into interior reservoirs of oil; it was, however, possible to simulate these effects by the use of solid plates of varying thickness and a standard porosity, made from earthenware.

F. G. Sawyer and D. F. Othmer<sup>68</sup> have described an apparatus for the rapid determination of equilibrium conditions between solid absorbents (activated charcoals) and the vapours of industrial solvents; they give a wide range of figures for typical cases.

An interesting device for removal of liquid in extraction processes has been patented<sup>69</sup> in which the solid is alternately treated with solvent under pressure, and put under reduced pressure for solvent removal. A special bubble-cap tower<sup>70</sup> for countercurrent liquid-liquid extraction has upright and inverted bubble caps on either side of each plate, and for the contact of gas with liquid<sup>71</sup> a wetted-wall tower has been built with a central rotor, which brings jets of the gas against the liquid films on the walls.

#### SEPARATION OF ISOTOPES.

It is considered timely to insert here a short summary of the work on bulk separation of isotopes, as described in the Government pamphlets on atomic energy.<sup>72</sup> Separation of heavy water was effected by well established methods of fractional distillation (light and heavy water differ in boiling point by  $1.4^{\circ}$ ) or by catalytic exchange reactions between hydrogen-deuterium mixtures and water. The isolation of  $^{235}\text{U}$ , or the enrichment of ordinary uranium in this isotope, was much more complicated. Three methods were more or less successful—electromagnetic, thermal diffusion, and porous barrier diffusion. The last appears to have been applied on the largest scale. All three were naturally not very selective, and a balance had to be struck between throughput and separation efficiencies, while a very large number of stages were necessary. For gaseous diffusion through a porous barrier, the hexafluoride naturally selected itself, and would appear to have been used. The essential difference in mass was only from 349 to 352, and the relative diffusion rates were therefore as 1.0043 to 1.0000. It has been suggested<sup>73</sup>

<sup>67</sup> *Trans. Amer. Inst. Chem. Eng.*, 1944, 40, 511; B., 1945, I, 83.

<sup>68</sup> *Ind. Eng. Chem.*, 1944, 36, 894; A., 1945, I, 56.

<sup>69</sup> U.S.P. 2,183,837; B., 1944, I, 349.

<sup>70</sup> U.S.P. 2,191,919; B., 1945, I, 206.

<sup>71</sup> B.P. 569,143; B., 1945, I, 280.

<sup>72</sup> "The Atomic Bomb" and "Atomic Energy." H.M.S.O.

<sup>73</sup> *Ann. Repts. Chem. Soc.*, 1944, 88 (cf. A. E. Brodski, *Acta Physicochim.*, U.R.S.S., 1942, 17, 224; A., 1944, I, 183).



that, for thermal diffusion, the amount of energy involved in a multi-stage process will be a very appreciable proportion of the energy available from fission of the  $^{235}\text{U}$  isolated. Data are not available for the ordinary diffusion method, but even using the 4000 stages which appear to be necessary it would not seem likely that anything approaching 1% of the atomic energy made available will be required for pumps and similar devices.

Reverting to the electro-magnetic method, it would appear that the ordinary operations of the mass spectrograph have been applied with some success, much greater separation efficiencies per stage being obtained than with the diffusion systems. The quantities involved are small, however, and methods for the separation of a charged beam of particles into clusters containing alternately light and heavy isotopes, which might have overcome this disadvantage, have not been effectively developed.

Thermal diffusion methods appear to have been uncertain in operation, but plants have been built to attempt the earlier stages of separation. The most successful process has been the diffusion of the hexafluorides through a porous barrier. The nature of this barrier and the precise methods of working remain a State secret. Methods of pumping and of recirculation through the various stages present a very complicated problem, and it will be of great interest to have, in due course, details of the pumps used.

#### MIXING.

A somewhat specialised form of mixing appears to be growing in popularity in catalytic gas reactions. J. C. Kalbach<sup>74</sup> describes as "fluidisation" the process whereby a solid material in finely divided form is suspended and maintained in turbulent motion by a stream of gas. The principle is used mainly in catalysis, and C. L. Thomas and J. Hoekstra<sup>75</sup> have indicated the advantages of such a catalyst bed in the avoidance of "hot spots" in exothermic reactions. Alternatively to suspension, the solid catalyst may be conveyed<sup>76</sup> continuously with the gas stream, and a portion drawn off continuously for regeneration.

J. P. Asquith<sup>77</sup> has made a general review of the process of mixing, and concludes that comprehensive data are available only for liquid-liquid and liquid-solid systems. He gives some typical cases from which a general law may be derived, and shows the possibility of waste of energy through splashing, vortices, and waves. S. A. Miller and C. A. Mann<sup>78</sup> have measured the power required in the agitation of two immiscible liquid phases; they find that such mixtures normally behave as though the viscosity is a geometric mean between the two individual

<sup>74</sup> *Chem. Met. Eng.*, 1944, **51**, No. 6, 94; B., 1944, I, 347.

<sup>75</sup> *Ind. Eng. Chem.*, 1945, **37**, 332; B., 1945, I, 242.

<sup>76</sup> U.S.P. 2,325,516; B., 1945, I, 244.

<sup>77</sup> *Trans. Inst. Chem. Eng.*, 1945; *Chem. and Ind.*, 1945, 47; cf. B., 1943, I, 263.

<sup>78</sup> *Trans. Amer. Inst. Chem. Eng.*, 1944, **40**, 709; B., 1945, I, 170.



viscosities, but that if a stable emulsion is formed, abnormal viscosity results also appear. It was necessary for efficient working that the agitator should be placed below the static separation line (i.e., in the heavy phase with the liquid at rest) but the form of the agitator did not appear to be important within fairly wide limits. A. Brothman, G. N. Wollan, and S. M. Feldman<sup>79</sup> suggest that, in a mixing operation, the completeness of dispersion approaches a limiting state in accordance with a logarithmic law; the constants are dependent on the system of stirring and on the phases being mixed, and they indicate methods for the analysis of mixing systems on these lines. A special centrifugal mixer<sup>80</sup> has been devised with a perforated plate inlet over which the centrifugal rotor moves, and thus gives a marked shearing action.

### DRYING.

The relative merits of "infra-red" and convective drying are still being discussed, and the issue is not made clearer by the rival advocates of gas and electric heating agents. C. C. Eeles<sup>81</sup> declares that convection ovens will be able to attain speeds as great as those claimed for infra-red plants. H. Silman<sup>82</sup> has measured the relative times required to heat up metal plates with various types of paint coating, using both electric lamps and gas-heated blocks as a source of heat. J. B. Carne<sup>83</sup> shows that the shape of objects being heated by radiation will have a very considerable effect on heat losses by convective currents; it is maintained that, with sharply curved surfaces, only convective heating can give uniform temperature distribution when articles of different curvatures are being heated in the same oven.

An attempt to employ high-frequency dielectric heating in the drying of vegetables has been described by E. Rushton, E. C. Stanley, and A. W. Scott.<sup>84</sup> The vegetables, in compressed blocks, could be heated readily to the desired temperature, but heating was very uneven and varied with the texture of the material; current consumption was considerable, and the process was found to be quite unsatisfactory. O. Krischer,<sup>85</sup> in an analysis of the moisture concentration fields produced in a porous solid during drying, concludes, rather surprisingly, that the rate of passage of air over the solid is relatively unimportant in drying; rates of drying are more readily affected by changes in the rate of heating or alterations in the external pressure.

It is sometimes a disadvantage that, in ordinary spray-drying, only one stage of working is possible, and high inlet air temperature or high air throughput per unit weight of liquid is required. A two-stage process

<sup>79</sup> *Chem. Met. Eng.*, 1945, 52, No. 4, 102.

<sup>80</sup> U.S.P. 2,321,599; B., 1945, I, 172.

<sup>81</sup> *Gas J.*, 1945, 246, 339.

<sup>82</sup> *Found. Tr. J.*, 1945, 75, 195; B., 1945, I, 274.

<sup>83</sup> *Gas J.*, 1945, 246, 435; B., 1945, I, 369.

<sup>84</sup> *Chem. and Ind.*, 1945, 274; B., 1945, III, 230.

<sup>85</sup> *Chem. Technik*, 1943, 16, 117; B., 1945, I, 313.



has been patented<sup>86</sup> in which humidity of the drying air is controlled; it is claimed to give greater throughput of solid per unit volume of drying space. The solid is air-conveyed between the stages, and does not come to rest before drying is complete. Another type of dryer,<sup>87</sup> in which the solid material is suspended in the air stream, uses the two cyclone forms set up in a long narrow cyclone separator to return partly-dried particles to the first (main drying) zone, while the second cyclone form entrains fully-dried dust and rejects the larger, partly-dried material. A very large gas-drying plant, handling 150 million cu. ft. of natural gas per day under a pressure of 1000 lb. per sq. in., has recently been described.<sup>88</sup> The dehydrating fluid was diethylene glycol, and the outlet dew point was reduced to 38° F.

#### FILTRATION AND GAS CLEANING.

D. R. Sperry<sup>89</sup> has maintained that practically all industrial slurries filter at constant pressure rates determined by the simple equation  $T = AQ + BQ^2$ ; he suggests that the constants  $A$  and  $B$  may be readily determined by experiment in the laboratory and applied directly in the design of full-scale plant. Suitable laboratory apparatus is described and a number of constants for typical slurries are listed. An easily cleaned rotary drum filter has been described,<sup>90</sup> in which the filter media are porous ceramic slabs, suitably curved and held to the frame by countersunk bolts.

In the field of gas cleaning, Calder-Fox scrubbers have been doing yeoman service in the war-time acid plants. G. L. Fairs<sup>91</sup> has given an account of the development of these scrubbers from the original series of plates with staggered orifices to a single pair of "orifice" and "impact" plates. These plates may be of lead, but are preferably of glass strips suitably arranged. As the clearance between the plates decreases, the distortion of the gas path increases and the size of particle that may be removed drops. The pressure drop goes up steadily at the same time, and limits are finally set by the tendency of the gas stream to re-entrain liquid from the edges of the strips. The smallest particle that may be removed is about 0.002 mm. in diameter, and formulæ are given for pressure drop and limiting particle size in various types of plant. Adaptations of the Calder-Fox system to the removal of solid particles were reviewed, and a patent<sup>92</sup> has described a rotating drum forming the impact surface, with a solvent washing off the precipitated solid. Another patent,<sup>93</sup> based on the same principle of rapid change in

<sup>86</sup> U.S.P. 2,312,474; B., 1945, I, 4.

<sup>87</sup> U.S.P. 2,316,207; B., 1945, I, 4.

<sup>88</sup> *Gas Times*, 1945, 44, 79.

<sup>89</sup> *Ind. Eng. Chem.*, 1944, 36, 323; B., 1944, I, 347.

<sup>90</sup> U.S.P. 2,306,074; B., 1945, I, 6.

<sup>91</sup> *Trans. Inst. Chem. Eng.*, 1945; B., 1945, I, 83.

<sup>92</sup> B.P. 562,394; B., 1944, I, 324.

<sup>93</sup> B.P. 569,866; B., 1945, I, 318.



direction, deals with specially formed channels to secure the maximum solid deposition in removing flue dust from fuel gases.

A special form<sup>94</sup> of dust-removal plant has been built in the form of a Venturi tube, in which the gases are set to swirl by suitable vanes and an outer layer, containing the bulk of the dust, is stripped off and passes to settling chambers; the cleaned gas re-enters the main stream as it passes into the divergent throat. Modifications of electrical precipitation include a long glass filament<sup>95</sup> with a sprayed metal coating acting as a discharge electrode; the roughness of the metal coating is claimed as an advantage. Other collecting electrodes<sup>96</sup> with a continuous film of liquid flowing downwards, or in two concentric shells, the inner one of which is perforated, have also been patented.

### MINERAL CONCENTRATION.

This branch of chemical technology has not been dealt with extensively in the Chemical Engineering section before. Such processes as flotation were described in reports on Non-Ferrous Metallurgy, to which fields they were largely confined. As indicated in the introduction to this report, methods of separation and concentration by the less obvious physical properties will clearly become more important and widespread. In the case of flotation, for instance, S. A. Falconer and B. D. Crawford<sup>97</sup> show that by a suitable choice of flotation agents it is possible to concentrate minerals such as tungstic oxide, manganese carbonate, and calcium sulphate to almost pure state. In many instances, densities of two substances differ fairly widely, and make a separation by float-and-sink methods possible if suitable liquids can be found. L. W. Needham and S. Lynch<sup>98</sup> have suggested that solid-liquid suspensions can now be prepared in stable form with densities up to 3.5 times that of water; a method hitherto confined to coal cleaning can thus enter a wider field.

G. D. Coe and W. H. Coghill<sup>99</sup> state that a laboratory jig washer can give a very accurate representation of the work of a large gravity concentration plant, and suggest that such a test can replace the laborious float-and-sink tests that are usually carried out. If this is so, it would appear that precision jigging will give as sharp a separation as float-and-sink methods for the separation of solids of different densities. A recently developed substitute for the jig washer is the Humphreys spiral,<sup>100</sup> in which a slurry flows rapidly down a spirally curved channel, banked at an acute angle to contain the fluid. In these conditions, heavy particles

<sup>94</sup> U.S.P. 2,322,414; B., 1945, I, 174.

<sup>95</sup> B.P. 568,343; B., 1945, I, 247.

<sup>96</sup> U.S.P. 2,192,249-50; B., 1945, I, 207.

<sup>97</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1754; B., 1945, I, 110.

<sup>98</sup> *Trans. Inst. Chem. Eng.*, 1945; B., 1945, I, 203.

<sup>99</sup> U.S. Bur. Mines, 1944, *Rept. Invest.* 3769; C., 1945, 66.

<sup>100</sup> Anon., *Chem. Met. Eng.*, 1945, 52, No. 4, 107.



collect at the inner edge of the spiral channel; the plant is said to be much more compact than the washing plant it replaces.

### SIZE REDUCTION.

A. M. Gaudin and R. T. Hukki,<sup>101</sup> using a special single-impact pendulum crusher, and employing gas adsorption for surface measurement, have shown that size distribution in a crushed solid is represented very closely by a straight line on a log size *vs.* log per cent. undersize plot. This linear relation is most clearly marked with the finer particles, and it is argued that the total surface in each of a series of size ranges of fixed ratio is a constant. This original work was carried out with quartz, and Gaudin, with S. S. Yavasca,<sup>102</sup> continued the investigation with galena, pyrites, and glass marbles. Their results appear to substantiate the previous findings.

An apparatus for measuring surface by the gas adsorption method has been described by Gaudin and F. W. Bowdish.<sup>103</sup> These methods for surface determination have been held by P. H. Emmett<sup>104</sup> to be the most reliable methods available. Measurements are made at low temperature and extrapolated back to give zero pressure determinations—the amount for a unimolecular layer. It is noted, however, that the results obtained are very close to those obtained by the permeability methods of Carman and others.

T. K. Prentice<sup>105</sup> has continued the discussion on the rate of ball wear in a ball mill, and still maintains that this rate is proportional to surface, and that therefore grinding must be by attrition and not by impact; arguing from this, he indicates the need for uniform spherical uniform balls in economic grinding. S. D. Michaelson<sup>106</sup> has proposed a method for laboratory determination of mill size when grinding a novel material. The grindability of the ore is compared with those of standard materials, and the probable power requirements are calculated from size reduction required and grinding figures from these laboratory tests; a mill is then chosen which will absorb that amount of power. A conversion from ball to rod grinding has been reported by H. R. Stahl<sup>107</sup>; the mill used was 6 ft. in diameter by 4 ft. long, and the rods charged were 4 ft. long and 1.75 in. in diameter. The mill was turned more slowly than when using a ball charge, but absorbed the same amount of power; the product had a narrower size range than the ball-ground material, and somewhat greater throughputs of a specific size product could be obtained than with a ball charge.

A. E. Reed<sup>108</sup> has compared the output of three typical grinding systems

<sup>101</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1779; B., 1945, I, 83.

<sup>102</sup> *Ibid.*, 1945, *Tech. Publ.* 1819; B., 1945, I, 242.

<sup>103</sup> *Ibid.*, 1944, *Tech. Publ.* 1666; B., 1944, I, 347.

<sup>104</sup> *Ind. Eng. Chem.*, 1945, 37, 639; C., 1945, 297.

<sup>105</sup> *J. Chem. Met. Soc. S. Africa*, 1944, 44, 179; B., 1944, I, 346.

<sup>106</sup> *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1844; B., 1945, I, 242.

<sup>107</sup> *Ibid.*, 1821; B., 1945, I, 242.

<sup>108</sup> *Ibid.*, 1820; B., 1945, I, 242.



when using the normal fluid classifying plant, and when using high-speed vibrating screens, the product being in each case of 100—200-mesh size range. The circulating load could be very much reduced when screens were used, and greater throughputs of the standard product could be obtained; following on this, smaller amounts of sub-sieve material were produced. The screens were of the Hummer and Tyrock types, with stainless steel cloths, but unfortunately power consumptions for screening and classifying were not stated.

A recent modification<sup>109</sup> of jet grinding utilises an "attrition" tube, of length upwards of 1000 times the internal diameter, through which the material is propelled by suitable gas jets. Patents<sup>110</sup> dealing with changes in the gyratory cone crusher show that this type of grinding unit is still developing, while further alterations in the shape of the swing-jaw crusher have also been described.<sup>111</sup> A roller grinding unit<sup>112</sup> of general form similar to the Raymond mill has been built with a rotating outer annular ring. The rollers are turned by friction with this ring and are retarded by electric generator brakes; as the speed of the mill increases, the torque of the brakes matches the increased centrifugal force and resulting friction. A series of rollers<sup>113</sup> form another crushing unit, in which only the bottom unit is power-driven; the other rolls are held against each other, and the bottom roll, in a vertical frame, by their own weight. The driving motion on the bottom roll is a rapid oscillation, and the inertia of the moving masses places a series of shearing stresses on material passing through the rolls. A control on ball-mill load has been devised<sup>114</sup> which makes an electrical condenser from a fixed nozzle just above the normal load level; the position of the load determines the capacity of this condenser and actuates the feeding system.

### MATERIALS.

A very comprehensive series of tests, spread over 15 years, on ordinary pipe-lines under various service conditions has been reported by C. F. Bonilla.<sup>115</sup> The lines were suspended in air or laid in moistened cinders, and were in use for steam or water. Not one of the various ferrous pipes used showed definite superiority for all purposes, and considerable variation in efficiency with conditions was observed. The Dow Chemical Company,<sup>116</sup> in a search for post-war outlets for magnesium metal, have developed a system of electrolytic pipe-line protection, in which blocks of magnesium alloy are buried in the earth some 10 ft. away from the pipe to be protected, and attached to it by suitable wiring. Twenty

<sup>109</sup> U.S.P. 2,315,083-4; B., 1944, I, 380.

<sup>110</sup> B.P. 567,299; U.S.P. 2,190,036; B., 1945, I, 171.

<sup>111</sup> B.P. 560,705; B., 1945, I, 315. U.S.P. 2,318,290; B., 1945, I, 115.

<sup>112</sup> U.S.P. 2,192,310; B., 1945, I, 208.

<sup>113</sup> B.P. 564,402; B., 1945, I, 5.

<sup>114</sup> U.S.P. 2,316,875; B., 1945, I, 5.

<sup>115</sup> *Trans. Electrochem. Soc.*, 1945, 87, 227; B., 1945, I, 241.

<sup>116</sup> *Chem. Eng. News*, 1945, 23, 984.



anodes, each 4 in. in diameter by 20 in. long, were used for a 41-mile stretch of 8-in. pipe.

C. G. Ollinger<sup>117</sup> has pointed out the numerous advantages of carbon blocks such as "Karbate." These materials can be rendered non-porous by suitable impregnation and are very easily machined to a true surface; this makes possible the construction of centrifugal pumps, pipes, and valves at a reasonable price. The material is resistant to thermal shock and to practically all non-oxidising corrosive agents. Thus carbon bricks have been used<sup>118</sup> in the construction of hot-gas flues for conveying fumes from metal-smelting furnaces, and a large Karbate cooler<sup>119</sup> for hydrochloric acid has functioned for four years without any maintenance requirements. Concerning this last, A. Lippman, jun.,<sup>119</sup> shows that heat-transfer rates up to 300 B.Th.U./sq. ft./hr./° F. have been obtained with an ordinary serpentine spray-cooled unit, and that in consequence the cooler has been very much smaller than the glass units it replaced.

D. W. Young and W. Harney<sup>120</sup> claim that polyisobutene tank linings are resistant to all inorganic liquids, with the exception of free halogens; for instance, such a lining is practically unattacked by anhydrous nitrating acid (15%  $\text{HNO}_3$  85%  $\text{H}_2\text{SO}_4$ ). The linings are made in sheets, and attached to the metal surfaces by a rubber cement, so that joints may be a source of weakness. The use of synthetic rubber of an oil-resistant type for packing glands of all types has been described by J. Forrest.<sup>121</sup> Neoprene G.N. is good for both hot and cold oil, but Hycar and Perbunan are better for cold oil alone. As an instance of war-time improvisation in Germany, H. Schmidt<sup>122</sup> has quoted the use of slag wool, compressed with a binder, as a joint gasket.

An interesting type of corrosion, which may be more common than is suspected, has been detected<sup>123</sup> in certain evaporator tubes. The liquid-vapour mixture moves in such tubes at a gradually increasing velocity as the proportion of vapour increases. H. Inglesent and J. A. Storrow show that this will create a "moto-electric" potential difference between top and bottom of the metal tube; their results on copper tubes taken from a glucose evaporator show that corrosion appears to follow on this induced e.m.f. Corrosion of pump shafts at the glands, combined with mechanical wear, is widespread in chemical works. S. L. Lopata has suggested<sup>124</sup> that this is often due to careless assembly and a poor choice of lubricants; as an instance of the latter, he points out that graphite greases will initiate an attack on stainless steels.

The troublesome tendency of many metals to develop brittleness at

<sup>117</sup> *Chem. Industries*, 1944, **54**, 683; B., 1945, I, 81.

<sup>118</sup> *Iron Steel Eng.*, 1944, **21**, Dec., 105.

<sup>119</sup> *Chem. Met. Eng.*, 1945, **52**, No. 3, 112; B., 1945, I, 254.

<sup>120</sup> *Ind. Eng. Chem.*, 1945, **37**, 675; B., 1945, II, 309.

<sup>121</sup> *Trans. Inst. Rubber Ind.*, 1945, **20**, 212; B., 1945, I, 274.

<sup>122</sup> *Stahl u. Eisen*, 1943, **63**, 360; B., 1945, I, 113.

<sup>123</sup> *J.S.C.I.*, 1945, **64**, 233; B., 1945, I, 346.

<sup>124</sup> *Chem. Met. Eng.*, 1944, **51**, No. 12, 104; B., 1945, I, 113.



low temperatures (below  $-40^{\circ}$ ) has been discussed by P. B. Petty,<sup>125</sup> who points out that pure element metals such as aluminium, lead, and nickel are least subject to this disadvantage; soldered joints are a particular source of trouble and should not be used in low-temperature work.

### BOILER WATER TREATMENT.

The problems of caustic embrittlement still call for considerable attention. H. N. Boetcher<sup>126</sup> notes that, in boilers working under very high pressures, a type of cracking occurs which very much resembles the effect of caustic alkali; the crack is always covered by a skin of hard dense magnetic oxide, and the lowest pressure at which it has been noted is 1200 lb. per sq. in. A discussion on previous papers<sup>127</sup> has brought out the indication that fatigue and local stress complicate the problem, whilst true caustic embrittlement is very localised as distinct from hydrogen embrittlement. H. Howard<sup>128</sup> has given an account of embrittlement effects observed many years ago in the manufacture of sodium aluminate, and overcome by the use of special steels.

R. T. Sheen and E. B. Woodruff<sup>129</sup> have shown how the normal lime-soda process may be modified to give a considerable degree of calcium removal with little or no magnesium precipitation. The pH of the mixture, after addition of the reagents, should be in the range 9.6–10.2, and the resulting water, after clarification, is quite soft enough for most industrial uses, although further treatment would be required for high-pressure boiler feeds. W. F. Gerrard<sup>130</sup> recommends that the normal lime-soda treatment be applied in two stages. In the first stage a considerable excess of lime can make magnesium precipitation more complete, while clarification should be assisted by the addition of paper pulp; in the second stage, excess of calcium hydroxide is removed by sodium bicarbonate. Times of treatment are much reduced, and residual hardness, with silica, is much lower than by the normal process, even when this is assisted by the use of sodium aluminate.

It has been suggested<sup>131</sup> that the volatilisation of certain inorganic salts in high-pressure boilers may be due to some type of solvent action by the steam. D. W. Rudorff has carried out experiments with a special autoclave designed to remove all entrained water and solid from the steam, and has traced a connexion between steam pressure and salt concentration in the condensate; there appears to be no such connexion between salt in the condensate and the concentration in the boiler. Although these facts might be explained by a solubility hypothesis, it seems more likely that hydrolysis of the salts, followed by ordinary

<sup>125</sup> *Chem. Met. Eng.*, 1945, 52, No. 6, 102; B., 1945, I, 345.

<sup>126</sup> *Mech. Eng.*, 1944, 66, 593; B., 1945, I, 138.

<sup>127</sup> *Proc. Inst. Mech. Eng.*, 1943, 150, 88; B., 1944, I, 378.

<sup>128</sup> *Chem. and Ind.*, 1944, 295; B., 1945, I, 2.

<sup>129</sup> *Ind. Eng. Chem.*, 1944, 36, 971; B., 1945, I, 82.

<sup>130</sup> *Manufg. Chem.*, 1945, 16, 64; B., 1945, I, 137.

<sup>131</sup> *Eng. Boiler House Rev.*, 1945, 59, 2; B., 1945, I, 82.



volatilisation, will account for the figures obtained. Rudorff<sup>132</sup> has also traced the effects of these solids in causing deposits on turbine blades; the first traces of deposit cause a pronounced drop in turbine efficiency, but further growth has little effect; this abnormality is ascribed to the roughening of the surface by the first layers of solid deposited, and is specific to individual materials (*i.e.*, silica causes more frictional loss than sodium chloride or sodium hydroxide).

A series of papers on corrosion inhibition has appeared, some of which are of interest in connexion with boiler water. U. R. Evans,<sup>133</sup> in a general review, shows that the best natural inhibitor is a sparingly soluble immediate product of corrosion; when the immediate product gives a secondary insoluble product attack will be promoted. Both "cathodic" and "anodic" inhibitors can be used, in suitable cases, but anodic inhibitors (formers of a sparingly soluble anodic product, or agents for increase of anodic polarisation), if unskilfully used, may promote intense local corrosion. The cathodic inhibitors are less efficient, but are not subject to such breakdown. R. S. Thornhill<sup>134</sup> gives details of the checking of steel corrosion with zinc and manganese salts, but adds a warning that both zinc and chromium salts can cause localised attack. G. B. Hatch and O. Rice<sup>135</sup> show, with reference to previous literature, how the addition of very small quantities (up to 5 p.p.m.) of a soluble phosphate (Calgon) prevents the deposition of calcium carbonate and ferric hydroxide scale from either hot or cold feed waters; despite this check, the corrosion of the iron surface is also inhibited, presumably by some type of phosphate scale in very thin layers. G. B. Hatch<sup>136</sup> has also given an account of the rate of formation of these phosphate films and methods of testing their efficiency. It is interesting to note, however, that S. T. Powell, H. E. Bacon, and J. R. Lill<sup>137</sup> recommend the deliberate deposition of calcium carbonate scale as a method for checking troublesome corrosion in water-cooling systems.

W. Stericker<sup>138</sup> has drawn attention to a simple method of preventing corrosion in water systems by the addition of small amounts (10—20 p.p.m.) of silica; this addition is carried out by the insertion in the feed line of a small tank containing a soluble glass. This treatment is particularly valuable in checking the preferential dissolution of zinc from brass pipes. C. G. Eldredge and R. B. Mears<sup>139</sup> discuss the use of inhibitors for corrosion of aluminium, and show that their action is very selective; thus chromium salts are effective in phosphoric but not in hydrochloric acid, whilst organic nitrogen compounds, such as acridine,

<sup>132</sup> *Eng. Boiler House Rev.*, 1945, 59, 61; B., 1945, I, 203.

<sup>133</sup> *Ind. Eng. Chem.*, 1945, 37, 703; B., 1945, I, 363.

<sup>134</sup> *Ibid.*, 706; B., 1945, I, 364.

<sup>135</sup> *Ibid.*, 710; B., 1945, I, 364.

<sup>136</sup> *Ibid.*, 752; B., 1945, I, 364.

<sup>137</sup> *Ibid.*, 842; B., 1946, I, 30.

<sup>138</sup> *Ibid.*, 716; B., 1945, I, 364.

<sup>139</sup> *Ibid.*, 736; B., 1945, I, 366.



show the reverse of this behaviour. The action of silicates in protecting from alkaline attack has long been known, while water may act as an inhibitor with certain almost anhydrous organic acids. In the checking of water corrosion with bimetallic systems, chromate solutions are the most commonly used inhibitors, according to M. Darrin,<sup>140</sup> and he lists a very large number of difficult cases where corrosion has been checked in this way, although the amount required may be rather high (up to 500 p.p.m.). A. Wachter<sup>141</sup> recommends the use of sodium nitrite in checking corrosion of metals by sodium chloride or organic alcohols in aqueous solution.

#### MISCELLANEOUS.

A collection of reports on the tendency, in large-scale production, to change from batch to continuous working has been published.<sup>142</sup> Conditions in which one or the other type of working seemed desirable were discussed, and various branches of the chemical industry were surveyed for possible developments in the future. Following on the previous mathematical treatments of continuous processing, H. M. Hulbert<sup>143</sup> has suggested that these continuous reaction systems may conveniently be used to determine activation energy and the order of the predominant reaction.

H. W. Cremer and R. L. Fitt<sup>144</sup> have discussed the siting and layout of chemical works; they indicate the influence of such factors as water and fuel supplies, transport and traffic handling, disposal of waste, and general administration. A review,<sup>145</sup> by M. F. Crass, of the methods of transport available for such dangerous chemicals as concentrated acids is entirely concerned with United States rules and methods. Nevertheless, much of the matter is of interest in this country; it is notable that the "balloon" type of carboy has been entirely replaced by a straight-sided vessel, and that detailed regulations for many types of rail tank are in force.

T. S. Murphy,<sup>146</sup> in an account of the use of rupture diaphragms, stresses the importance of calculating the probable rate at which pressure will build up in a reaction unit, and providing a large enough diaphragm for discharge at this rate after bursting. The vapours from such a burst disc may constitute a fire risk, one of the many indicated by W. F. Cooper and F. H. Mann<sup>147</sup> in their survey of specific hazards in chemical plant; they list a number of particularly notable risks, and give a series of tables of flash points and spontaneous ignition temperatures.

<sup>140</sup> *Ind. Eng. Chem.*, 1945, 37, 741; B., 1945, I, 364.

<sup>141</sup> *Ibid.*, 749; B., 1945, I, 363.

<sup>142</sup> *Chem. Met. Eng.*, 1945, 52, No. 5, 101.

<sup>143</sup> *Ind. Eng. Chem.*, 1944, 36, 1012; B., 1945, I, 81.

<sup>144</sup> *Trans. Inst. Chem. Eng.*, 1945.

<sup>145</sup> *Chem. Eng. News*, 1945, 23, 16; B., 1945, I, 113.

<sup>146</sup> *Chem. Met. Eng.*, 1944, 51, No. 12, 99; B., 1945, I, 113.

<sup>147</sup> *J. Inst. Elect. Eng.*, 1944, 91, Part I, 267; B., 1944, I, 377.

E. J. Heeley,<sup>148</sup> in a paper on Class I welded vessels for pressure stresses, points out that specifications are still based on the strength of riveted joints; he proposes a simple formula of the "thin wall" type for use in general design. J. R. Kritschewski and D. Tziklis<sup>149</sup> have given some account of the problems of design for very high pressures (up to 10,000 atmospheres).

H. Griffiths<sup>150</sup> has proposed a standard notation method in physico-chemical calculation. The dimensional forms are disentangled from the "numerics," or non-dimensional numbers, throughout the calculation; the limits of accuracy of any accepted equation should be set out, together with the proper fields of application. A standard notation of simple form is given for the method. H. G. MacColl<sup>151</sup> has urged the necessity for statistical methods of control in routine analysis, and given details of their application in metallurgical work. U. R. Evans<sup>152</sup> also indicates the importance of some mathematical check on the errors inherent in a series of observations.

<sup>148</sup> *Trans. Inst. Mech. Eng.*, 1944.

<sup>149</sup> *J. Phys. Chem. Russ.*, 1943, 17, 115; B., 1945, I, 49.

<sup>150</sup> *Chem. and Ind.*, 1945, 338; B., 1946, I, 2.

<sup>151</sup> *Ibid.*, 1944, 418.

<sup>152</sup> *Ibid.*, 1945, 106; B., 1945, I, 169.



## FUEL.

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THE cessation of the war with Germany and Japan has brought no relief to the position created by the shortage of solid fuel: there has been no amelioration of the rationing of coal for both domestic and industrial purposes. In this country there was an all-round increase of 3s. 6d. per ton in the price of coal on 1st May; this means that the average pithead price is now 38s. per ton, compared with 18s. in 1939. A new Act<sup>1</sup> which makes the Ministry of Fuel and Power permanent charges the Minister "with the general duty of securing the effective and co-ordinated development of coal, petroleum and other minerals and sources of fuel and power in Great Britain, of maintaining and improving the safety, health and welfare of persons employed in or about mines and quarries therein and of promoting economy and efficiency in the supply, distribution, use and consumption of fuel and power, whether produced in Great Britain or not": by-products also come under the Ministry. Coal production figures, down to the first quarter of this year, have been published<sup>2</sup>: during 1944, the output of deep-mined coal (184,098,000 tons) fell 5%; half this loss was compensated by the increase in the output of open-cast coal (8,647,000 tons). The decline continued in 1945, the first quarter's production being 3½% below that of the corresponding quarter of 1944. There has been a continued growth in the quantity of coal used for generating electricity and a further decline in that available for domestic consumers. The second quarter of 1945<sup>3</sup> showed a further decrease in output compared with the first quarter of the year (1·8 million tons) and with the second quarter of 1944 (2·4 million tons). Between 1940 and 1944 domestic consumption of coal fell by 11 million tons (8·5 million tons net after deducting an amount equivalent to the increased domestic consumption of coke, gas, and electricity) compared with an estimated saving by rationing of 10 million tons, in a full year, of all kinds of fuel in terms of coal.<sup>4</sup> The annual consumption of coal of all kinds in domestic premises in one year (1944—45) was 35·8 million tons: exact figures of the percentage of the energy content of this coal usefully used are not available but the Minister of Fuel and Power optimistically estimated the average to be in the neighbourhood of 20%<sup>5</sup>; a figure for the thermodynamic efficiency would be even more illuminating.

<sup>1</sup> *Inst. Fuel, War Time Bull.*, 1945, Apr., 178.

<sup>2</sup> *Statistical Digest 1944*, H.M. Stat. Off., Cmd. 6039; see also *Times*, 29th May, 1945; *Gas J.*, 1945, 245, 690; *Gas World*, 1945, 122, 521.

<sup>3</sup> *Iron and Coal Tr. Rev.*, 1945, 151, 299.

<sup>4</sup> *Coll. Guard.*, 1945, 170, 745.

<sup>5</sup> *Ibid.*, 615.



The Trade Association Fuel Efficiency Committees have made valuable contributions to the national fuel economy campaign and the Ministry's Fuel Efficiency Committee have issued a single document containing all the information so far available from the following industries: cement, lime burning, cocoa and chocolate, cake and biscuit, bronze and brass, ironfounding, rayon and silk, and laundry.<sup>6</sup>

Statistics of the coal production in other countries are again being released. The Union of South Africa has been exporting more coal than any other country in the world: production in 1943 was more than 22 million tons: in 1943—44, shipments from two ports amounted to 3.7 million tons. Australian output in 1944 was 14 million tons.<sup>7</sup> Data concerning the production of brown and hard coal by individual German collieries in 1936—37 have also been given.<sup>8</sup> The history and distribution of ownership and output of the French coal mines have been reviewed and the conditions obtaining during the period 1939—44 described<sup>9</sup>: a state-owned organisation, the Houillères Nationales du Nord et du Pas-de-Calais, controlling two thirds of the French coal mines was formed on 13th December, 1944. Production totals for France during the years of occupation were as follows: 1941, 43.9; 1942, 43.8; 1943, 42.5; 1944, 40.6 million tons. Cost of production rose steeply and the production per miner per shift averaged 958 kg. against 1206 kg. in 1939.

The Report of the Hydrocarbon Oil Duties Committee<sup>10</sup> recommended that chemical manufacturers be allowed to receive without payment of duty, as raw material for chemical synthesis, any imported oil and that oils produced from indigenous material and used for the same purpose shall be subsidised by an amount equal to the duty payable on like, imported oils. In 1944, 100.3 million gallons of crude benzole and 2.1 million tons of tar were produced from coal.<sup>11</sup>

The symposium on thermal insulation arranged by the Institute of Fuel has made an important contribution to the fuel efficiency campaign: the following subjects were reviewed and discussed: the properties and processes which control the flow of heat in continuous and intermittent heating operations, by H. R. Fehling<sup>12</sup>; the economics of saving fuel, by G. N. Critchley<sup>13</sup>; the practical aspects of reheating and heat-treatment furnace insulation, by A. Stirling<sup>14</sup>; the thermal insulation of buildings, by N. S. Billington<sup>15</sup>; heat losses and the insulation of open-hearth furnaces and blast furnaces, by J. M. Ferguson<sup>16</sup>; thermal insulation

<sup>6</sup> *J. Inst. Fuel*, 1945, 18, 89.

<sup>7</sup> *Coll. Guard.*, 1945, 171, 96.

<sup>8</sup> *Coll. Eng.*, 1945, 22, 139.

<sup>9</sup> *Engineer*, 1945, 180, 26.

<sup>10</sup> H.M. Stat. Off., *Cmd.* 6615, 1945.

<sup>11</sup> *Coll. Guard.*, 1945, 170, 615.

<sup>12</sup> *J. Inst. Fuel*, 1944, 18, 15.

<sup>13</sup> *Inst. Fuel, War Time Bull.*, 1944, Oct., 16; *B.*, 1945, I, 1.

<sup>14</sup> *J. Inst. Fuel*, 1944, 18, 39.

<sup>15</sup> *Ibid.*, 1945, 18, 62.

<sup>16</sup> *Inst. Fuel, War Time Bull.*, 1945, Apr., 141; *B.*, 1945, I, 201.



as applied to pottery furnaces, kilns, and carbonising plant, by J. S. F. Gard<sup>17</sup>; insulation of heat-treatment furnaces, by R. J. Sarjant<sup>18</sup>; the thermal insulation of boilers was also discussed<sup>19</sup> and additional shorter papers were contributed at the final meeting of the conference.<sup>20</sup> A similar symposium on industrial waste heat recovery is being arranged by the Institute.

The Institute of Fuel and the National Smoke Abatement Society have issued a report<sup>21</sup> on a Joint Conference on atmospheric pollution by industrial and domestic coal users. In his Chadwick Public Lecture,<sup>22</sup> Dr. A. Parker gave figures for atmospheric pollution caused by smoke, ash, and sulphur dioxide emitted by industrial and domestic fuel users and by railways and electricity generating stations. In his Dunn Memorial Lecture<sup>23</sup> Dr. M. P. Applebey discussed the history of atmospheric pollution and modern means of minimising it.

The Engineers' Report to the Minister of Fuel and Power on the Severn Barrage Scheme has been published.<sup>24</sup>

A notable publication during the year was the "Chemistry of Coal Utilisation," edited by H. H. Lowry,<sup>25</sup> a two-volume book written by experts and covering a wide range of aspects of coal properties and utilisation.

#### FUEL RESOURCES.

The Ministry of Fuel and Power has issued a number of Regional Survey Reports<sup>26</sup> drawn up by committees under the chairmanship of the Ministry's respective Regional Controllers: these reports, which are concerned with the character and reserves and the methods of mining coal, deal with the Durham, Kent, Midland (Cannock Chase, Warwickshire, South and North Staffordshire, and Shropshire), North Midland (Nottinghamshire, North and South Derbyshire, and Leicestershire), North-Eastern (Yorkshire), North-Western (Lancashire, Cheshire, and North Wales), and Northumberland and Cumberland coalfields. The Director of Fuel Research, Dr. A. Parker,<sup>27</sup> has made a brief statement of the main conclusions to be drawn from the data collected by the Regional Valuation Boards: during the next 100 years it should be possible to maintain an average annual output from all our coalfields of 200 million tons with approximately the same distribution of types of coal as at present; a possible shortage of good coking coals may be met by

<sup>17</sup> *Inst. Fuel, War Time Bull.*, 1945, Apr., 151; B., 1945, I, 201.

<sup>18</sup> *Ibid.*, June, 189.

<sup>19</sup> *Ibid.*, 203.

<sup>20</sup> *J. Inst. Fuel*, 1945, 19, 19.

<sup>21</sup> *Report on Joint Conference, Inst. Fuel and Nat. Smoke Abatement Soc., London*, 1945.

<sup>22</sup> *Engineering*, 1945, 159, 273.

<sup>23</sup> *Chem. and Ind.*, 1945, 298.

<sup>24</sup> H.M. Stat. Off., 1945.

<sup>25</sup> John Wiley and Sons, Inc., New York, 1945, Vols. I and II.

<sup>26</sup> H.M. Stat. Off., 1945.

<sup>27</sup> *J. Inst. Fuel*, 1945, 18, 158.



advances in carbonisation technique. J. H. Jones<sup>28</sup> has described the coal seams and outlined the physical and chemical characteristics of the coals of Northumberland and Durham. The work of the Coal Survey of the Fuel Research Board (D.S.I.R.) in the coalfields of Warwickshire, Staffordshire, Worcestershire, Shropshire, and the Forest of Dean has been described by F. Scarf.<sup>29</sup> R. A. Mott<sup>30</sup> has related the rank of the coals in the Yorkshire, Nottinghamshire, and Derbyshire coalfield to their depth: the deeper seams, particularly in the west, are of higher rank and are more likely to be of coking quality.

A new coalfield to the east and south-east of Lincoln has been discovered during oil-boring operations: several thick seams have been proved beneath 3000 ft. of rocks.<sup>31</sup> A Fowler<sup>32</sup> has reported that boring operations at the south-western corner of the Cleveland Hills showed the presence of some thin coal seams at a depth of between 4316 and 4348 ft.

H. G. Raggat<sup>33</sup> in a survey of Australia's mineral industry has stated that bituminous coal is well distributed over Queensland and New South Wales, which have fair reserves, as has also Tasmania; in Victoria the known reserves of lignite are large and in South Australia considerable lignite deposits have been proved.

Estimated reserves and proximate analyses of the coals in several Chinese coalfields have been published.<sup>34</sup> T. Y. Chong<sup>35</sup> has given a general and concise survey of China's coal industry: the total coal reserves are estimated at 248,187 million tons; 6.2% of this is suitable for metallurgical purposes; the total output in 1943 was well over 70 million tons.

The U.S. Bureau of Mines has issued technical papers on the carbonising properties of coals from Western Region, Interior Province,<sup>36</sup> Pocahontas No. 3 bed, Kimball, McDowell County,<sup>37</sup> Columbus No. 4 mine and Hardburly mine, Perry County,<sup>38</sup> and from Willow Creek coal bed, Kemmera District, Lincoln County.<sup>39</sup> A. J. Johnson<sup>40</sup> has discussed United States anthracites and semi-anthracites and D. H. Davis and J. Griffin<sup>41</sup> have reviewed the properties, distribution, reserves, and composition of the Pittsburgh coal seam in Pennsylvania, which produces about 14% of American coal output: reserves are estimated at 7500 million metric tons. Extensive analytical information on Kentucky

<sup>28</sup> *Inst. Fuel, War Time Bull.*, 1945, Feb., 89; B., 1945, I, 117.

<sup>29</sup> *Ibid.*, Aug., 255; B., 1945, I, 376.

<sup>30</sup> *Trans. Inst. Min. Eng.*, 1945, 104, 446; B., 1946, I, 52.

<sup>31</sup> *Gas J.*, 1945, 245, 211.

<sup>32</sup> *Geol. Mag.*, 1944, 81, 193, 254.

<sup>33</sup> *Bull. Imp. Inst.*, 1944, 44, 279.

<sup>34</sup> *Bull. Geol. Survey China*, No. 33.

<sup>35</sup> *Min. J.*, 1945, 224, 214, 348.

<sup>36</sup> *U.S. Bur. Mines, Tech. Paper* 667; B., 1945, I, 89.

<sup>37</sup> *Ibid.*, 670; B., 1945, I, 89.

<sup>38</sup> *Ibid.*, 672; B., 1945, I, 247.

<sup>39</sup> *Ibid.*, 673; B., 1945, I, 247.

<sup>40</sup> *Trans. Amer. Inst. Min. Met. Eng.*, 1944, 157, 11.

<sup>41</sup> *Ibid.*, 22.



coals, Virginia coals, and Pennsylvanian anthracite coals has been published by A. C. Fieldner and co-workers.<sup>42</sup>

F. A. Botschkovski<sup>43</sup> and V. I. Fomenko and S. A. Pantschenko<sup>44</sup> have reported on coals of the Donetz basin and B. I. Kustov<sup>45</sup> on those of the Tas-Komyrsay deposit. A. Michailov<sup>46</sup> has given an account of new Russian coal resources in the north and east.

Analyses, calorific values, and the results of low-temperature assays of some Indian coals have been published by S. C. Shome and N. V. V. Parthasarathi.<sup>47</sup>

C. A. P. Southwell<sup>48</sup> has reviewed the development of the small oilfield at Eakring (Notts.) and the work on the small wells at Formby (Lancs.) and at Hardstoft.

#### COAL MINING AND PREPARATION.

The Report of the Technical Advisory Committee set up by the Ministry of Fuel and Power, under the chairmanship of C. C. Reid, to advise on what changes are necessary to bring the coal mining industry to a state of full technical efficiency has been issued<sup>49</sup>: the Report makes it clear that neither natural conditions nor the coal-cutting methods employed are responsible for the low output of British mines. Inefficient methods of underground transport of both coal and miners and the lack of any proper system of training for entrants into the industry are all important factors contributing to the present unsatisfactory position. F. A. Burchardt,<sup>50</sup> from a statistical study of the size and productivity of coal mines in Great Britain, has found that mines of 1000 workers and more show a productivity above the average and that productivity also varies according to districts.

A comprehensive survey of the information available on the development of underground gasification of coal in Russia up to 1944 has been made by L. J. Jolley and N. Booth<sup>51</sup>: the available Russian data on this subject have been analysed by E. T. Wilkins.<sup>52</sup>

G. S. Scott<sup>53</sup> has discussed exhaustively the behaviour and control of anthracite mine fires. The use of the konimeter in assessing concentrations of airborne coal dust has been described by W. Staton,<sup>54</sup> and N. M. Potter<sup>55</sup> has discussed the principles involved in sampling such dusts.

The equipment used in open-cast coal mining in Western Missouri,

<sup>42</sup> U.S. Bur. Mines, *Tech. Papers* 652, 656, 659.

<sup>43</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **44**, 111; B., 1945, I, 175.

<sup>44</sup> *Geol. Zhur.*, 1940, **7**, No. 4, 33.

<sup>45</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 388; B., 1945, I, 117.

<sup>46</sup> *Coll. Guard.*, 1945, **170**, 445.

<sup>47</sup> *J. Indian Chem. Soc., Ind. Ed.*, 1944, **7**, 149; B., 1945, I, 319.

<sup>48</sup> *J. Inst. Petroleum*, 1945, **31**, 27; B., 1945, I, 144.

<sup>49</sup> H.M. Stat. Off., 1945.

<sup>50</sup> *Bull. Inst. Statistics*, 1944, **6**, 15.

<sup>51</sup> *Fuel*, 1945, **24**, 31, 73; B., 1945, I, 284.

<sup>52</sup> *Fuel Econ. Rev.*, 1944, **23**, 14.

<sup>53</sup> U.S. Bur. Mines, 1944, *Bull.* 455; B., 1945, I, 9.

<sup>54</sup> *Coll. Guard.*, 1944, **168**, 707; B., 1944, I, 384.

<sup>55</sup> *Coll. Eng.*, 1944, **21**, 85, 107; B., 1944, I, 384.



where the production is estimated at 1 million tons of washed coal per year, has been described by M. Read.<sup>56</sup> C. W. H. Holmes<sup>57</sup> has reported that as a coal outcrop is approached there is a gradual fall in calorific value, caking power, and sulphur content: the properties and production of open-cast coal in the North Midland Region have been described by A. Dawe.<sup>58</sup>

*Cleaning.*—The increasing use of mechanical appliances for mining and handling coal has necessitated a wider use of coal-cleaning plant. G. S. Jenkins<sup>59</sup> and R. C. Smart<sup>60</sup> have reviewed methods of coal cleaning. A. Holdsworth<sup>61</sup> has given operating data for two coal-screening and Rheolaveur washing plants and G. Mullin<sup>62</sup> has described a plant operating in County Durham which has a capacity of 130 tons per hour and is a combination of the Barvoys gravity-washer with the Hoyois washer. E. Trümpelmann<sup>63</sup> has studied, in the laboratory, new methods of coal washing in dense media: ground rolling-mill scale was found to be the most economical and suitable material for the suspension, giving satisfactory efficiency for the  $+\frac{1}{4}$ -in. coal but not for the fines. Float-and-sink determinations have been carried out by the U.S. Bureau of Mines<sup>64</sup> using bath densities at intervals of 0.01 in order to explore the possibility of separating exceptionally clean coal fractions. J. O. Samuels<sup>65</sup> has stated that large quantities of fine coal can be recovered from washery water by means of a starch-salt hydrate flocculating agent.

A Conference of the Institute of Fuel<sup>66</sup> has discussed the qualities of coal required by the various sections of industry in this country, together with the problems involved in the preparation of these qualities by the coal industry: a paper on coal preparation was contributed by a committee; H. C. Applebee, H. H. Thomas, and T. A. Tomlinson discussed the coal requirements of the gas industry; H. C. Armstrong those of the iron and steel industry; a number of engineers, those of the electrical industry: papers on coal supply and the appliance maker, locomotive coal, and the performance of shell-type boilers were contributed by P. A. H. Elliot, M. G. Bennett, and E. G. Ritchie, respectively, and there was also a paper on the mechanical stoker and the utilisation of coal.

R. L. Brown<sup>67</sup> has reviewed the types of coals used in various industries giving particular attention to coal sampling.

*Briquetting.*—V. F. Parry<sup>68</sup> has given an account of a technical and

<sup>56</sup> *Min. Congr. J.*, 1945, **31**, 18.

<sup>57</sup> *Inst. Fuel War Time Bull.*, 1945, *Apr.*, 167; *B.*, 1945, **I**, 208.

<sup>58</sup> *Ibid.*, *Aug.*, 245; *B.*, 1945, **I**, 376.

<sup>59</sup> *J. Inst. Fuel*, 1945, **18**, 109; *B.*, 1945, **I**, 209.

<sup>60</sup> *Coll. Eng.*, 1945, **22**, 15, 28; *B.*, 1945, **I**, 209.

<sup>61</sup> *Iron Coal Tr. Rev.*, 1945, **150**, 87, 125, 166; *B.*, 1945, **I**, 282.

<sup>62</sup> *Ibid.*, 1944, **149**, 982; *B.*, 1945, **I**, 247.

<sup>63</sup> *Glückauf*, 1943, **79**, 529, 559; *B.*, 1945, **I**, 282.

<sup>64</sup> *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3812; *B.*, 1945, **I**, 319.

<sup>65</sup> *Inst. Fuel War Time Bull.*, 1945, *Feb.*, 103; *B.*, 1945, **I**, 118.

<sup>66</sup> *J. Inst. Fuel*, 1945, **18**, 94–109, 113; *B.*, 1945, **I**, 209.

<sup>67</sup> *Brit. Coal Utilisation Res. Assoc. Bull.*, 1944, **8**, 317; *B.*, 1945, **I**, 143.

<sup>68</sup> *U.S. Bur. Mines*, 1944, *Rept. Invest.* 3757; *B.*, 1944, **I**, 353.



economic study of a packaged fuel which consisted of paper-wrapped cubical briquettes of slack : 10—20 lb. of starch per ton, and also asphalt and Portland cement, were used as binders : calorific values, compressive strengths, and abrasive properties were also measured. K. Sauberlich<sup>69</sup> has studied the stability of brown-coal briquettes. The substitution of coal by charcoal, uneconomic in some parts of the world, is not necessarily so where coalfields are distant and where wood, otherwise useless, can cheaply be turned into charcoal. A method of making charcoal briquettes by a hand-operated drop stamp has been described by H. Greene and T. N. Jewitt.<sup>70</sup> The briquetting is done on a cold wet charcoal-pitch mixture ; gum arabic is used as a primary binder. The products are a satisfactory substitute for coal in stationary furnaces. A satisfactory substitute for coal for locomotives was made using drop stamps and charcoal ground in edge-runner mills.

#### PHYSICAL AND CHEMICAL PROPERTIES OF COAL.

The coefficient of restitution of a number of coals has been measured by C. G. Cannon and W. H. George,<sup>71</sup> by dropping small steel spheres on to a plane polished surface of the specimen : the results obtained indicated that energy is absorbed by permanent elastic deformation and also by some other mechanism in the case of low-rank bright coals. The infra-red ( $1\ \mu.$  to  $14\ \mu.$ ) absorption spectra of a thin coal section, of coal extracts, and of humic acids have been obtained by C. G. Cannon and G. B. B. M. Sutherland<sup>72</sup> : these indicate the presence of the following groups : OH (with hydrogen bonding), CH (aliphatic and aromatic), C:O (in humic acids),  $-C:C:C:C-$  in aromatic rings, and  $CH_2$  and  $CH_3$  groups. R. E. Brewer<sup>73</sup> has roughly correlated the fluidity (Gieseler max.) of 19 U.S.A. semi- and sub-bituminous coals with their rank and studied the effect of the various petrographic constituents on this property : the fluidity is abnormally increased by anthraxylon, translucent attritus, and cannel, and decreased by opaque attritus, fusain, ash, and high oxygen content.

H. E. Blayden, J. Gibson, and H. L. Riley<sup>74</sup> have continued their X-ray diffraction studies into the crystallographic nature of coal and coal fractions, and have shown that certain vat dyes, *e.g.*, dibenzanthrones, on carbonisation, behave in a manner similar to that shown by highly caking coals : their X-ray results do not confirm the claims of some to have synthesised bituminous coal in the laboratory. C. R. Kinney<sup>75</sup> has found that several bituminous coals and lignites with volatile matter contents ranging from 16 to 46% all yield an approximately constant percentage of methane on carbonisation under the same conditions : the yield of methane from peat, lignin, and some lignites is less than for

<sup>69</sup> *Braunkohle*, 1943, 42, 233 ; B., 1945, I, 282.

<sup>70</sup> *J.S.C.I.*, 1945, 64, 266 ; B., 1946, I, 9. See also *Nature*, 1944, 154, 58.

<sup>71</sup> *Nature*, 1945, 155, 787.

<sup>72</sup> *Trans. Faraday Soc.*, 1945, 41, 279 ; A., 1945, I, 184.

<sup>73</sup> *Ind. Eng. Chem.*, 1944, 36, 1165 ; B., 1945, I, 118.

<sup>74</sup> *Inst. Fuel War Time Bull.*, 1945, Feb., 117 ; B., 1945, I, 144.

<sup>75</sup> *Fuel*, 1945, 24, 16 ; B., 1945, I, 118.



bituminous coals, whilst for carbohydrates it is lower still: this is taken to support the view that coal is derived from lignin rather than cellulose. J. J. Ward, W. R. Kirner, and H. C. Howard<sup>76</sup> have studied the alkaline permanganate oxidation of certain condensed cyclic organic compounds and coal and found a qualitative correlation between their respective rates of oxidation and their "double bond characters." A parabolic relation between the course of oxidation in air and the time for certain coals was found by W. A. Frey,<sup>77</sup> who also reported that high pyrites (contrary to the commonly accepted view) and ash contents retard, and high ferrous oxide content accelerates, the take-up of oxygen.

A review of the action of chemical reagents on bituminous coal has been given by G. H. Thomson,<sup>78</sup> F. Roll<sup>79</sup> has criticised the Donath-Bode method of distinguishing brown from bituminous coal, and H. Brusset<sup>80</sup> has given an account of the chemical constituents of peat.

*Solvent Extraction.*—The action of solvents on coal has a twofold importance, viz., (a) it offers a means of breaking down the coal substance into simpler fractions which either may have a commercial value or may be of theoretical interest in teaching more about the ultimate molecular character of coal, or (b) provided a cheap and efficient enough solvent is available it offers a relatively simple means of converting a solid into a liquid fuel. V. I. Zabavin<sup>81</sup> has studied the reaction of coal with benzoic anhydride. (Mlle.) M. Cassel<sup>82</sup> has found that amyl alcohol extracts a larger bitumen fraction from a number of lignites and coals than does the more usually employed alcohol-benzene mixture; the addition of 5% aqueous hydrochloric acid increased its solvent action, in one case 45.5% of the coal being dissolved. The action of solvents on torbanite and the nature of the soluble products obtained have been investigated by J. A. Dulhanty.<sup>83</sup> M. K. Djakova and N. V. Melenteeva<sup>84</sup> have shown that solubility in tetrahydronaphthalene at 400° decreases with the rank of the coal and also in the order, clarain > vitrain > durain > fusain: coals containing 41% of volatile matter yielded 63–70% of soluble fraction. A Gillet<sup>85</sup> has discussed the chemical processes involved in the extraction of coal with anthracene oil at 350°, the reaction of the soluble fraction with oleic acid, and also the decomposition of coal in an inert gas stream at 350–600°. Tetralin, anthracene oil, mazout, and a pressure-hydrogenated residue have been employed at 400–420° by M. K. Djakova<sup>86</sup> to extract 40–45% of the total organic matter in peat

<sup>76</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 246; A., 1945, II, 230.

<sup>77</sup> *Oel u. Kohle*, 1943, **39**, 603; B., 1945, I, 282.

<sup>78</sup> *Brit. Coal Utilisation Res. Assoc. Bull.*, 1944, **8**, 258; B., 1945, I, 283.

<sup>79</sup> *Braunkohle*, 1942, **41**, 596; C., 1945, 15.

<sup>80</sup> *Bull. Soc. chim.*, 1943, [v], **10**, 109; B., 1945, I, 144.

<sup>81</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1943, Part 8, 35; B., 1945, I, 10.

<sup>82</sup> *Compt. rend.*, 1943, **216**, 445; B., 1945, I, 10.

<sup>83</sup> *J. Proc. Roy. Soc. New South Wales*, 1943, **76**, 268; B., 1945, I, 10.

<sup>84</sup> *J. Appl. Chem. Russ.*, 1943, **16**, 296; B., 1945, I, 54.

<sup>85</sup> *Rev. univ. Mines*, 1943, **19**, 147; B., 1945, I, 283.

<sup>86</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 408; 1943, **40**, 194; B., 1945, I, 54, 10.



in the preparation of liquid motor and boiler fuel. C. M. Cawley and J. G. King<sup>87</sup> have made a survey of British wax-bearing lignites and peats in order to obtain an indigenous source of high-melting wax in place of German montan wax: the peat waxes were found to have lower melting points and higher acid and ester values than lignite wax or montan wax. According to S. I. Gusev<sup>88</sup> the sulphur content of Russian coal bitumens obtained by extraction with pyridine, aniline, and quinoline is of the order 2—3%, a value which did not vary much with different solvents: all the sulphur in the chloroform-soluble fraction of the aniline extract was in the form of diphenylene sulphide.

*Coal Tar.*—The identification of the products of its thermal decomposition offers another means of learning something of the molecular nature of coal. The following compounds have been isolated from various tars: 4-hydroxyhydrindene from coal tar by E. Kahles<sup>89</sup>; 2:6-dimethylquinol from cracked Estonian' shale tar by V. A. Lanin and M. S. Gorocholinskaja<sup>90</sup>; a large number of alkyl-substituted pyridines from a sapropelite tar by V. A. Lanin and E. A. Poshiltzova<sup>91</sup>; 1:12-benzperylene from coal-tar pitch by J. W. Cook and N. Percy,<sup>92</sup> and 7-azaindole from coal tar by O. Kruber,<sup>93</sup> who has also reviewed the progress of coal-tar research in the period 1910—40.<sup>94</sup> D. W. Milner<sup>95</sup> has discussed the uses and prospects of the organic compounds separable from coal tar. J. Reilly, P. Moynihan, and D. Reilly<sup>96</sup> have studied peat-tar oils with particular reference to their bactericidal power, and J. C. Aherne and J. Reilly<sup>97</sup> have described the emulsifying power of Irish peat wax. The formation of molecular compounds of phenol, cresol, and xylenol with pyridine has been studied by H. Wille<sup>98</sup> in an attempt to explain why both types of compounds are present in tars. J. W. Cook, N. Percy, and J. M. Robertson<sup>99</sup> have confirmed the presence of *n*-hentriacontane in the wax fraction of Scottish shale oil.

*Humic Acids.*—Our fuller knowledge of the molecular nature of coal awaits the elucidation of the structure of those complex substances, the humic acids and the humins. The state in which humic acids are present in alkaline solution has been investigated by G. Bouilloux<sup>100</sup> by studying the changes in various properties of the solutions, such as viscosity, light absorption, and electrical conductivity, brought about

<sup>87</sup> *J.S.C.I.*, 1945, 64, 237.

<sup>88</sup> *Chem. Age*, 1945, 52, 401.

<sup>89</sup> *Ber.*, 1942, 75, [B], 1313; *B.*, 1944, I, 386.

<sup>90</sup> *J. Appl. Chem. Russ.*, 1943, 16, 47; *B.*, 1945, I, 55.

<sup>91</sup> *Ibid.*, 388; *B.*, 1945, I, 119.

<sup>92</sup> *J.S.C.I.*, 1945, 64, 27; *B.*, 1945, I, 119.

<sup>93</sup> *Ber.*, 1943, 76, [B], 128; *A.*, 1945, II, 68.

<sup>94</sup> *Brit. Coal Utilisation Res. Assoc. Bull.*, 1945, 9, 126.

<sup>95</sup> *J. Inst. Fuel*, 1945, 18, 80; *B.*, 1945, I, 144.

<sup>96</sup> *Sci. Proc. Roy. Dublin Soc.*, 1944, 23, 239; *B.*, 1945, I, 90.

<sup>97</sup> *Ibid.*, 247; *B.*, 1945, I, 90.

<sup>98</sup> *Brennstoff-Chem.*, 1942, 23, 271.

<sup>99</sup> *J.S.C.I.*, 1945, 64, 26; *B.*, 1945, I, 119.

<sup>100</sup> *Bull. Soc. chim.*, 1944, [v], 11, 38; *A.*, 1946, II, 60.



by the gradual addition of sodium carbonate. H. B. Charmbury, J. W. Eckerd, J. A. La Torre, and C. R. Kinney<sup>101</sup> have experimented on the humic acids obtained by oxidising coal with nitric acid and have found that the nitrogen in these acids is present in two states: the greater part is in a highly oxidised state and is liberated as nitrate ion by permanganate oxidation; the remainder is liberated as ammonia by alkaline permanganate oxidation and hydrolysis; the former is probably present in nitro-groups and the latter in nitroso- or oximino-groups.

*Inorganic Constituents.*—F. H. Gibson and W. A. Selvig<sup>102</sup> have reviewed the occurrence of rare and uncommon elements in coal: more than half of the known elements are reported as occurring in coal but in amounts which are considered too low to warrant industrial recovery. In a survey of New Zealand coals, T. A. Rafter<sup>103</sup> has found that the average boron content of the coal ash for each coalfield varies from 0.06 to 1.09%: an ash containing 1.3% of strontium oxide was also found. H. E. Crossley<sup>104</sup> has continued his investigations into the fluorine content of coals; in samples from all the British coalfields it has been found to range from nil to 175 p.p.m., and to bear no relationship to the amount of chlorine or ash: the fluorine appears to be present as a fluorapatite. The industrial significance of the results has also been studied. V. M. Ratinski<sup>105</sup> has found that in Caucasian coals germanium is concentrated mainly in the vitrain, the ash of which contains 0.1–1.0%. I. P. Alimarin<sup>106</sup> has reviewed the methods of determining germanium in coal ash and G. I. Egorov<sup>107</sup> has reported analyses of coal ashes from the Donetz basin. R. F. J. Teichmann<sup>108</sup> has studied the atmospheric oxidation of pyrites associated with South African coals. J. R. Arthur and K. D. Wadsworth<sup>109</sup> have reviewed the effect of inorganic compounds on the behaviour of coals and cokes and A. H. Edwards<sup>110</sup> their effect on the calculation of calorific values from ultimate analyses.

### CARBONISATION.

*Blending.*—The physical and chemical changes occurring during carbonisation are so complex and the variables so numerous that it is difficult to lay down, except in general terms, the principles on which the blending of coking slacks should be based: it is now widely recognised, however, that provided the agglutinating constituents are present in sufficient proportion, the addition, to the blend, of relatively inert materials such as coke breeze and anthracite, in a sufficiently finely-divided state,

<sup>101</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 625; A., 1945, II, 288.

<sup>102</sup> *U.S. Bur. Mines*, 1944, *Tech. Paper* 669.

<sup>103</sup> *Nature*, 1945, **155**, 332.

<sup>104</sup> *J.S.C.I.*, 1944, **63**, 289, 342; B., 1945, I, 9, 54.

<sup>105</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **40**, 198; B., 1945, I, 9.

<sup>106</sup> *Trans. All-Union Conf. Anal. Chem.*, 1943, **2**, 371; C., 1945, 157.

<sup>107</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **43**, 19; B., 1945, I, 118.

<sup>108</sup> *J. Chem. Met. Soc. S. Africa*, 1945, **45**, 141; B., 1945, I, 282.

<sup>109</sup> *Brit. Coal Utilisation Res. Assoc. Bull.*, 1944, **8**, 296; B., 1945, I, 143.

<sup>110</sup> *Ibid.*, 328; B., 1945, I, 247.



will bring about some improvement in the physical characteristics of the coke. W. Seymour and L. D. Schmidt<sup>111</sup> have reported experiences at 21 coking plants on the effect of blending anthracite fines with coking slack: 10 plants reported favourably, 4 unfavourably, and 7 were neutral: they considered that many of the plants could substitute 3—5% of the anthracite fines for the same proportion of low-volatile coal without serious effect on blast-furnace operation. D. L. Newkirk<sup>112</sup> has reported that the substitution of 5—6% of a hard anthracite (volatile matter 4%) for some of the low-volatile coal in the blend gave a coke which was larger, stronger, harder, and more blocky and brittle than that from the normal blend: there was increased production of breeze but the performance in the blast furnace was satisfactory. According to J. G. Clendenin, K. M. Barclay, and C. C. Wright<sup>113</sup> pulverising and heating the anthracite to 950° before blending tend to increase the strength of the resultant coke, the size of which is greater when coarser anthracite is used. H. A. Brassert & Co.<sup>114</sup> have claimed that it is possible to make a hard, abrasion-resistant coke by mixing finely-divided (less than 40-mesh) anthracite or other non-caking coal with 10—25% of dry, finely-divided pitch or bitumen and carbonising the mixture spread in a uniform layer over the floor of a coke oven which is heated from below to 650—1100°.

*Coking Practice.*—Variations in the moisture content of the incoming coal cause fluctuations in the bulk density of oven charges and result in the production of non-uniform coke, in unsteady operating conditions, and in possible damage to ovens by occasional excessively high bulk densities. W. S. Landers, L. D. Schmidt, and W. Seymour<sup>115</sup> have studied the variation of the bulk density of coking slack, with and without the addition of 0.2 and 0.5 gal. of 26° A.P.I. petroleum coal spray oil per ton of coal: addition of oil was found to reduce the effect of the moisture on the bulk density. The bulk density of the oiled coal exceeded that of the unoiled except at low moisture content, when the unoiled coal showed excessively high and dangerous bulk density. The importance of maintaining the water content of coking coals as constant and as low as possible has been emphasised by G. Blecher,<sup>116</sup> who has studied the dependence of heating requirements on the bulk density of the charge and the effects of blending fractions of different size and of different moisture content and has recommended a maximum moisture content of 8—10% according to the quality and size of the coal.

J. G. King, D. MacDougall, and H. Bardgett<sup>117</sup> have found that increasing the free space in horizontal retorts, by reducing the charge,

<sup>111</sup> U.S. Bur. Mines, 1945, Rept. Invest. 3808; B., 1945, I, 248.

<sup>112</sup> Blast Furn. and Steel Plant, 1945, 33, 461; B., 1946, I, 158.

<sup>113</sup> Trans. Amer. Soc. Mech. Eng., 1945, 67, 405; B., 1946, I, 158.

<sup>114</sup> B.P. 563,366; B., 1944, I, 356.

<sup>115</sup> U.S. Bur. Mines, 1945, Rept. Invest. 3807; B., 1945, I, 248.

<sup>116</sup> Glückauf, 1944, 80, 125; B., 1945, I, 283.

<sup>117</sup> Gas J., 1945, 246, 259, 263; B., 1945, I, 320.



increased the yield of gaseous therms because of the longer cracking time : at first the increase was not at the expense of the tar therms, which also increased, but eventually the tar yield fell and its free carbon content increased. A van Ahlen<sup>118</sup> has shown that if the temperature in the gas-collecting space of a coke-oven battery is reduced to a value below the normal level, benzole of inferior quality is produced and the yield of commercial products from the benzole is reduced. Various procedures for increasing the yield of valuable by-products have been reviewed by L. Nettlenbusch,<sup>119</sup> in particular, a means of minimising the thermal decomposition of tar vapours. R. J. Barritt<sup>120</sup> has discussed the advantages of the Beimann main and quotes results obtained on two German plants before and after its installation. The same author and D. T. Barritt<sup>121</sup> have stressed the importance for design purposes of a proper knowledge of the changes of pressure due to flow in the combustion flues and regenerators and have indicated the lines along which development of heating-flue systems has taken place.

The war-time production at gas works of reactive coke suitable for mobile producers has been described by H. D. Greenwood and J. G. King and by T. F. E. Rhead and E. T. Pickering.<sup>122</sup> The former have found that coals of caking power between the limits C and G.2<sup>123</sup> yield reactive cokes and are available in quantity. By carbonising such coals in continuous vertical retorts at temperatures about 50° below normal and with throughputs 15—20% greater than normal, cokes having a critical air blast (C.A.B.) value about 0.04 can be produced. The latter carbonised moderately-caking, low-rank coals in vertical retorts, with 8—14% steaming at temperatures slightly below normal, with maximum throughput compatible with full carbonisation. The cut and screened product was activated by heating it to 120° and spraying it with 18% aqueous sodium carbonate solution and drying : its C.A.B. value was  $0.04 \pm 0.01$ . They also discussed the feasibility of replacing the nation's petrol supplies by reactive fuels.

G. C. Soth and C. C. Russell<sup>124</sup> have measured the pressures obtained when various coals and coal blends are carbonised in a test oven provided with a movable wall : the pressure seems to be a consequence of the resistance offered to the escape of volatile matter by that portion of the coal which is present in a highly viscous state. They found that it was possible to predict with a reasonable degree of certainty the type of pressure curve from the results of laboratory tests requiring less than 1 lb. of coal.

<sup>118</sup> *Glückauf*, 1942, **78**, 259 ; see also *Gas Times*, 1945, **44**, 77.

<sup>119</sup> *Ibid.*, 1943, **79**, 33 ; B., 1945, I, 283.

<sup>120</sup> *Coke*, 1945, **7**, 25 ; B., 1945, I, 281.

<sup>121</sup> *Gas World (Coking Sect.)*, 1945, **33**, 5.

<sup>122</sup> *Inst. Gas Eng.*, 1945, *Comm.* 281 ; B., 1945, I, 248 ; see also *Gas World*, 1945, **44**, 631 ; *Coke*, 1945, **7**, 179.

<sup>123</sup> Cf. B., 1944, I, 385.

<sup>124</sup> *Trans. Amer. Inst. Min. Met. Eng.*, 1944, **157**, 281.



G. A. Phillipson<sup>125</sup> has outlined the apparatus and technique for the repair of coke-oven walls by spray-welding, which involves the fusion of the cement employed by means of an oxy-acetylene flame. He has also<sup>126</sup> described the cleaning, by means of compressed air injected through special blowing tubes, of coke-oven regenerators which had become partly blocked owing to deposition of dust from the blast-furnace gas used for heating.

H. Zollikofer<sup>127</sup> has given the results of full-scale carbonisation tests on peat, coal-peat, paper, leather, and bituminous shale, and F. Frank<sup>128</sup> has described means of producing metallurgical coke and town's gas from peat. Shortage of coal at Niort (France) in 1941 necessitated the use of walnut logs, and M. P. Blanc<sup>129</sup> has described their carbonisation in Glover-West retorts.

*Coke.*—R. K. Dutta Roy<sup>130</sup> has studied the physico-chemical properties of cokes prepared by carbonising ten coals from the Jharia coalfield (India) in boxes embedded in full-scale oven charges, and H. Hock<sup>131</sup> has investigated the water absorption of various cokes and finds that coke quenched at a high temperature contains a higher percentage of water than that quenched at a low temperature.

*Graphite.*—The graphitisation of lampblacks has been studied by U. Hofmann, M. von Ardenne, A. Ragoss, F. Sinkel, and R. Holst.<sup>132</sup> Samples of various carbon blacks were heated for prolonged periods at temperatures up to 3000° and the crystallite growth was followed by means of X-ray diffraction; the changes in the secondary aggregates (particle size and shape) were followed by electron microscopy and the changes in adsorptive properties by means of experiments with methylene-blue. The results obtained have an important bearing on our knowledge of the crystallographic character of carbon. H. L. Riley<sup>133</sup> has reviewed the chemistry and X-ray crystallography of graphite and its lamellar compounds.

#### COMBUSTION.

*Solids.*—A detailed, comprehensive, and critical review by H. Guérin<sup>134</sup> on the reactions of carbon with carbon dioxide, oxygen, and water vapour has been published: some 551 references up to 1941 are cited. The development of more efficient and economic methods of separating

<sup>125</sup> *Coke*, 1945, 7, 45; B., 1945, I, 283.

<sup>126</sup> *Ibid.*, 148; B., 1946, I, 159.

<sup>127</sup> *Schweiz. Ver. Gas- u. Wasserfachm. Monatsbull.*, 1943, 23, 249; B., 1945, I, 209.

<sup>128</sup> *Coke*, 1944, 6, 231; B., 1945, I, 248.

<sup>129</sup> *Gas J.*, 1945, 246, 133; B., 1945, I, 284.

<sup>130</sup> *Quart. J. Geol. Min. Soc. India*, 1943, 15, 179; B., 1945, I, 283.

<sup>131</sup> *Braunkohle*, 1942, 41, 48; B., 1945, I, 283.

<sup>132</sup> *Kolloid-Z.*, 1941, 96, 231; A., 1944, I, 145. *Ibid.*, 1943, 105, 118; B., 1944, I, 354. *Z. physikal. Chem.*, 1941, B, 50, 1; A., 1944, I, 145.

<sup>133</sup> *Fuel*, 1945, 24, 8, 43; A., 1945, I, 156.

<sup>134</sup> "Le Problème de la Réactivité des Combustibles Solides," Dunod, Paris, 1945.



gases has given rise to further investigations into the practicability of burning solid fuels in oxygen or oxygen-enriched air. J. Körting<sup>135</sup> has described the effects of oxygen enrichment on combustion conditions and concluded that it would only be economic for certain special high-temperature furnaces. J. B. Fortune,<sup>136</sup> from data on 18 U.S.A. blast furnaces, concludes that it is doubtful whether or not dehydration of the blast is really beneficial; he has also reviewed experiments on the use of oxygen-enriched blast. According to W. Lennings<sup>137</sup> output may be increased by up to 30% by the use of oxygen-enriched blast, which would lead to an economic reduction in production costs.

The reactions which occur when coke is burned in the cupola and the manner in which the physical and chemical properties of the coke affect cupola operation have been discussed by B. P. Mulcahy.<sup>138</sup> J. Roberts<sup>139</sup> has measured the ignition temperatures of coals and cokes and discussed his results in relation to the ease of ignition of these fuels in the domestic grate. The rate of combustion of coke has been measured by E. Orosco<sup>140</sup> by direct determination of the loss in weight of a burning sample; he found that in the initial stages the loss in weight is proportional to the time. A. A. Skotschinski, S. Z. Makarov, and T. V. Rode<sup>141</sup> have studied the tendency of coal for self-ignition by a differential method: two endothermic effects at 50—60° and 80—140° were usually observed and these were taken to indicate the evaporation of loosely- and of firmly-bound moisture; at higher temperatures an exothermic effect due to the oxidation of the coal substance was observed. D. J. W. Kreulen<sup>142</sup> has claimed to have shown that the formation of carbon dioxide and water in the oxidation of coal by means of gaseous oxygen can take place independently of the formation of humic acids. R. E. Jones and D. T. A. Townend<sup>143</sup> have given an account of an experimental study of the behaviour of typical coals during oxidation, employing an adaptation of Yule and Wilson's method of estimating peroxygen, and have discussed their results in relation to the causes of spontaneous oxidation of stored coal.

*Vapours and Gases.*—The war-time shortage of matches has led to a greatly increased use of lighters; E. W. Steinitz<sup>144</sup> has studied the efficiencies of a number of pure liquids as lighter fuels and found that cyclohexane gave the best results. H. Velde<sup>145</sup> has found that the octane

<sup>135</sup> *Gas- u. Wasserfach.*, 1943, **86**, 377; B., 1945, I, 1.

<sup>136</sup> *Metallurgia*, 1944, **30**, 152; B., 1945, I, 31.

<sup>137</sup> *Stahl u. Eisen*, 1943, **63**, 757; B., 1945, I, 158.

<sup>138</sup> *Trans. Amer. Found. Assoc.*, 1945, **52**, 819; B., 1945, I, 210.

<sup>139</sup> *Coke*, 1944, **6**, 211; B., 1945, I, 284.

<sup>140</sup> *Anais Assoc. Quím. Brasil*, 1944, **3**, 197; C., 1945, 165.

<sup>141</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1944, **29**; B., 1945, I, 55.

<sup>142</sup> *Rec. trav. chim.*, 1943, **62**, 215; B., 1945, I, 175.

<sup>143</sup> *Nature*, 1945, **155**, 424.

<sup>144</sup> *Petrol Times*, 1944, **48**, 604; B., 1945, I, 286.

<sup>145</sup> *Oel u. Kohle*, 1944, **40**, 10; B., 1945, I, 321.



number of various petrols falls during storage as a result of an increase in the peroxide content; inhibitors can prevent peroxide formation. According to W. A. Herbst<sup>146</sup> the addition of 1—2% of a methyl or ethyl halide to petrol raises the closed-cup flash point to a temperature above 51°, so rendering the petrol less likely to accidental ignition. C. F. Kettering<sup>147</sup> has reviewed the effect of the molecular structure of fuels on the power and efficiency of internal-combustion engines, with special reference to triptane ( $\beta\beta\gamma$ -trimethylbutane). E. M. Nygaard, J. H. McCracken, and F. M. Seger<sup>148</sup> have claimed that the cetane number of a Diesel fuel is increased from 50 to 60.5 by the addition of 1% of a compound made by the interaction of trichloromethyl chlorothiol ( $\text{CCl}_3\cdot\text{SCl}$ ) and phenol in the presence of 2N. caustic soda.

D. T. A. Townend's<sup>149</sup> Jubilee Memorial Lecture to the Glasgow and Birmingham Sections of the Society was concerned mainly with modern aspects of gaseous combustion; slow combustion, critical explosion limits, and inflammability ranges were among the topics discussed. W. T. David<sup>150</sup> has made some interesting studies of gaseous explosions in spherical bombs; temperature and pressure measurements were consistently less than the theoretically calculated values. This energy defect, which amounted to as much as 15% of the energy of the reaction, was apparently due to the formation of carbon dioxide molecules of abnormal structure which lost this excess energy as visible radiation on contact with a catalytically active surface. W. J. Walker<sup>151</sup> has devised a method of computing the temperature and pressure of combustion of a fuel-air mixture, taking into account dissociation and reassociation. According to G. Damköhler and R. Edse<sup>152</sup> the composition of the gas mixture formed in the combustion in air of a fuel containing carbon and hydrogen may depend on 10 equations and 10 unknowns; they have suggested a procedure for solving such equations.

G. Whittingham<sup>153</sup> has found that the addition of small amounts of sulphur dioxide to a luminous smoky flame decreased the luminosity, and with 5% of sulphur dioxide a blue flame was given which deposited sulphur on cooled surfaces: the addition of small amounts of sulphur trioxide increased the luminosity of such flames; a fully aerated flame was made luminous by the addition of about 1% by volume of sulphur trioxide. R. H. Baulk<sup>154</sup> has reviewed the methods and means of measuring flame emissivity.

<sup>147</sup> *Ind. Eng. Chem.*, 1945, **36**, 1079; B., 1945, I, 118.

<sup>148</sup> U.S.P. 2,327,708; B., 1945, I, 324.

<sup>149</sup> U.S.P. 2,326,102; B., 1945, I, 324.

<sup>150</sup> *Chem. and Ind.*, 1945, 346.

<sup>151</sup> *Proc. Inst. Mech. Eng.*, 1944, **151**, 236; B., 1945, I, 55.

<sup>152</sup> *Phil. Mag.*, 1944, [vii], **35**, 680; B., 1945, I, 91.

<sup>153</sup> *Z. Elektrochem.*, 1943, **49**, 178; B., 1945, I, 119.

<sup>154</sup> *Nature*, 1945, **156**, 207; A., 1946, I, 223.

<sup>155</sup> *Brit. Coal Utilisation Res. Assoc. Bull.*, 1945, **9**, 33.



## MANUFACTURED AND SUBSTITUTE FUELS.

The world shortage of fuel and shipping has led to an increased use of substitute fuels particularly for internal-combustion engines. J. G. King<sup>155</sup> has reviewed the prospects of substituting imported petroleum products by colloidal fuel, petrol from coal, liquid methane, and reactive coke. W. D. Spencer<sup>156</sup> has summarised and drawn various conclusions from a series of previously published papers on coal-in-oil conversion. A. van Itterbeck<sup>157</sup> has discussed the use of methane as a motor fuel and stated that a litre of the liquefied gas is equivalent to 0.7 litre of petrol; the use of natural- and sewage-gas containing 70—95% of methane and also of town's gas as motor fuels has been described by F. Eckert.<sup>158</sup> A. C. Egerton and M. Pearce<sup>159</sup> have enumerated the advantages to be gained by using liquid methane as a fuel for internal-combustion engines and given data obtained from trials carried out on commercial vehicles: they have pointed out that the engineering problems connected with the use of liquid methane include the design of a suitable storage tank, of an evaporator, and of a fuel/air mixer and have described the sources and methods of production of liquid methane.

G. Egloff and M. Alexander<sup>160</sup> have assessed the possibilities of the use of methane, town's gas, propane and butane, acetylene, hydrogen, and ammonia as substitute motor fuels and C. Stiasni<sup>161</sup> has also discussed by-product propane-butane mixtures. E. Kroch<sup>162</sup> has reported favourably on the use in Belgium of anhydrous ammonia, with coal gas as ignition promoter, as a motor fuel.

*Hydrogenation.*—A. C. Fieldner, H. H. Storch, and L. L. Hirst<sup>163</sup> have found that, in general, the banded bright coals, from high-volatile bituminous to lignitic inclusive, are suitable for hydrogenation, whilst anthracites, semi-bituminous, splint, and cannel coals and coals rich in fusain are less so. According to W. Klempt<sup>164</sup> anthracite can be so changed by sulphurisation followed by ionic exchange with certain metalloids that it is converted by hydrogenation into a material which resembles a fat coal as regards its composition and coking properties.

*Fischer-Tropsch Synthesis.*—J. T. Eidus and N. D. Zelinski<sup>165</sup> have argued that carbides are not intermediate products in the Fischer-Tropsch synthesis since the reaction velocity of their formation is very much less than that of hydrocarbon formation: they have given experimental evidence of the intermediate formation of  $\text{CH}_2$  radicals. J. T.

<sup>155</sup> *J. Inst. Fuel*, 1944, **17**, 192; B., 1944, I, 355.

<sup>156</sup> *Petroleum*, 1944, **7**, 184; B., 1944, I, 387.

<sup>157</sup> *Brennstoff u. Wärmewirts.*, 1943, **25**, 54; B., 1945, I, 287.

<sup>158</sup> *Oel u. Kohle*, 1943, **39**, 237; B., 1945, I, 287.

<sup>159</sup> *J. Inst. Fuel*, 1945, **18**, 161, 193; B., 1945, I, 351.

<sup>160</sup> *Petrol. Refiner*, 1944, **23**, 235; B., 1945, I, 11.

<sup>161</sup> *Oel u. Kohle*, 1943, **39**, 650; B., 1945, I, 287.

<sup>162</sup> *J. Inst. Petroleum*, 1945, **31**, 213; B., 1945, I, 321.

<sup>163</sup> *U.S. Bur. Mines*, 1944, *Tech. Paper* 666; B., 1945, I, 143.

<sup>164</sup> *Glückauf*, 1942, **78**, 387.

<sup>165</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1942, 190; B., 1945, I, 176.



Eidus<sup>166</sup> has investigated Fischer-Tropsch catalysts and postulated separate active centres on the surface for the reaction with carbon dioxide and for the hydrogenation of carbon monoxide. According to V. I. Komarewsky and C. H. Riesz<sup>167</sup> the American gas industry is contemplating the use of water-gas plants in off-peak periods for the Fischer-Tropsch synthesis. W. Grimme<sup>168</sup> has described German developments in the Fischer-Tropsch process: low-boiling products are recovered from the exit gases by means of active carbon; catalysts have been developed for (1) the dehydrogenation of propane and butane (chromium oxide, aluminium oxide), (2) the conversion of normal butene into isobutane (phosphoric acid), and (3) the conversion of normal butane into isobutane (aluminium chloride and hydrochloric acid).

*Coal-in-Oil.*—From laboratory and field tests on coal-in-oil fuels for boiler furnaces, J. F. Barkley, A. B. Hersberger, and L. R. Burdick<sup>169</sup> have concluded that combustion efficiency is slightly less than when using oil fuel. V. F. Kustov and L. L. Chotuntzev<sup>170</sup> have examined the viscosity of coal-fuel oil suspensions and found that it increases rapidly with increase in concentration of the disperse phase, but not in a linear fashion: optimum concentrations of coal for technical application are 30–40%; concentrations of 50% yield mixtures which are non-fluid at ordinary temperatures. R. M. Bridgwater<sup>171</sup> has made an exhaustive review of the literature of colloidal fuel and has attempted to estimate the future possibilities with regard to its use. Developments in the use of colloidal fuel in Russia have also been reviewed.<sup>172</sup>

*Power Alcohol.*—W. L. Owen<sup>173</sup> has discussed the production of motor fuel from molasses, particularly from the economic viewpoint: pure culture yeasts increase the yield, ensure constancy of operation, and enable adaptation to molasses of widely varying composition; small additions of manganous sulphate appear to be essential for realising high yields.

#### GAS PRODUCERS.

The British Standards Institution,<sup>174</sup> co-operating with the Ministries of Fuel and Power and of War Transport, has drawn up standard methods of testing fuels available in the country for mobile producers. The tests included are for moisture, potential tar, ash, sulphur and chlorine contents, and for critical air blast value. E. Thurn<sup>175</sup> has examined the oils from vehicles operated on producer gas and reported that when the producer

<sup>166</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1944, 255, 349; A., 1945, I, 250.

<sup>167</sup> *Petrol. Refiner*, 1944, 23, 91.

<sup>168</sup> *Chem. Trade J.*, 1945, 117, 289.

<sup>169</sup> *Trans. Amer. Soc. Mech. Eng.*, 1944, 66, 185; B., 1944, I, 388.

<sup>170</sup> *Symp. Visc. Liquids and Colloids, Acad. Sci. U.R.S.S.*, 1941, 1, 405; *J. Inst. Petrol.*, 1945, 31, 322A.

<sup>171</sup> *Petroleum*, 1945, 8, 2.

<sup>172</sup> *Eng. Boiler House Rev.*, 1945, 59, 226.

<sup>173</sup> *Sugar*, 1944, 39, No. 2, 24; No. 4, 26; B., 1944, I, 355; 1945, I, 176.

<sup>174</sup> *Brit. Standard* 1264, 1945.

<sup>175</sup> *Oel u. Kohle*, 1943, 39, 772; B., 1944, I, 386.



fuel is wood, the oils contain 1.5% of ash, and when brown-coal briquettes, not less than 3% of ash; alkali oxides, sulphates, silicates, and phosphates were detected in the ash: the author also discussed means of gas filtration. P. Steffan<sup>176</sup> has described the down-draught Evers-Union mobile producer which operates on brown-coal briquettes and E. Rammler<sup>177</sup> the Imbert, Zeuch, Wisco, Kröning, Bur, and Mercedes-Benz producers. F. van Lierde<sup>178</sup> has described mobile producers and compared the results obtained using producer gas from wood and charcoal with those obtained using liquid fuel. Details have been given of the methods used in converting some hundreds of Dutch fishing vessels to Diesel-producer gas operation using anthracite as the producer fuel.<sup>179</sup> A. P. Oleson and R. Wiebe<sup>180</sup> have calculated the thermodynamic properties of two typical producer-gas mixtures with particular reference to their use in internal-combustion engines.

A. Rozinck<sup>181</sup> has given an account of the construction and working of the Szikla-Rozinck "suspension" producer which he claims can use coal of 0—5 mm. size without previous preparation or grinding, does not require a grate, is insensitive to changes in the nature and quality of the coal, and permits 40% of the ash to be removed in liquid form. E. M. Brown<sup>182</sup> has reported that anthracite nuts (0.375—1.5 in.) gave satisfactory service in a 6-ft. hand-operated producer and would tolerate the addition of 50% of peas (100% 0.625 in. with 50.4% 0.25 in.) whereas the latter alone was unsatisfactory; corrosion by washer water was reduced by the addition of sodium carbonate rather than by lime. G. Dougill<sup>183</sup> has discussed the cleaning of producer gas and means of overcoming difficulties occasioned by the short-circuiting of an electrostatic precipitator by deposited ash, tar, and sodium chloride. A Melbourne plant using briquetted Morwell brown coal and giving a gas of calorific value 370 B.Th.U. per cu. ft. has been described by A. S. Fitzpatrick<sup>184</sup>; carburetting with tar or oil increased the calorific value to 500—520; enrichment by catalytic conversion of the carbon monoxide into methane is under consideration. A. Thau<sup>185</sup> has reviewed the progress made during the last two decades in the production of producer gas, water-gas, and synthesis gas.

#### FURNACES AND BOILERS.

The formation of encrustations on boiler tubes and heating surfaces is an important factor in the loss of thermal efficiency and is receiving

<sup>176</sup> *Braunkohle*, 1943, **42**, 377; B., 1945, I, 11.

<sup>177</sup> *Ibid.*, 353; B., 1945, I, 11.

<sup>178</sup> *Brennstoff u. Wärmewirts.*, 1943, **25**, 1; B., 1945, I, 11.

<sup>179</sup> *Trans. Inst. Mar. Eng.*, 1944, **56**, 127.

<sup>180</sup> *Ind. Eng. Chem.*, 1945, **37**, 653.

<sup>181</sup> *Arch. Wärmewirts.*, 1943, **24**, 51; B., 1945, I, 11.

<sup>182</sup> *Ind. Chem.*, 1944, **20**, 552; B., 1944, I, 385.

<sup>183</sup> *Inst. Chem. Eng. and Chem. Eng. Group (Soc. Chem. Ind.)*, 1945, *Advance Copy*; B., 1945, I, 90.

<sup>184</sup> *Chem. Eng. Min. Rev.*, 1945, **37**, 175; B., 1945, I, 249.

<sup>185</sup> *Teer u. Bitumen*, 1943, **41**, 139; B., 1945, I, 284.



an increasing amount of attention. J. R. Rylands and J. R. Jenkinson<sup>186</sup> have reviewed the theories as to the nature and formation of these deposits on economiser tubes and air heaters in stoker-fired water-tube boilers; on the basis of their experiments the authors suggest that the deposits result from the interaction of concentrated sulphuric acid with some of the alumina compounds in the fly-ash and also indicate means of preventing such deposits. E. Schumann<sup>187</sup> has described means of removing these encrustations and suggested that the cleaned surface should be treated with a graphite emulsion to render it smooth and retard clinker formation. A. Zinsen<sup>188</sup> has examined and classified about 200 bituminous-coal ashes and some brown-coal ashes, on the basis of their respective contents of refractory oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ), iron oxides ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ), and residual oxides ( $\text{CaO}$ ,  $\text{SO}_3$ , etc.), into five types which vary in their tendency to form deposits on boiler heating surfaces and refractory walls: fayalite ( $2\text{FeO}, \text{SiO}_2$ ) may play an important part in the formation of these deposits because it lowers the sintering temperature of the ash; the evolution of silicon monosulphide and disulphide may also be important because if they are not oxidised they may condense and form a sticky layer. L. M. Clark and J. Haslam<sup>189</sup> have examined by chemical and X-ray analysis a deposit from the fireside of an economiser and found it to contain 4.5% of boron phosphate. The corrosion of furnace-wall tubes in pulverised-fuel-fired boilers of American central power stations has become acute and an investigation sponsored by the U.S. Bureau of Mines and the Combustion Engineering Company has been carried out by W. T. Reid, R. C. Corey, and B. J. Cross<sup>190</sup>; they examined 16 furnaces in 13 stations and found that the deposits were mainly of two types: (1) a bluish-white sulphate "enamel" soluble in water, giving an acid reaction and consisting principally of a solid solution of sodium and potassium sulphates and alkali-metal ferric trisulphates, e.g.,  $\text{K}_3\text{Fe}(\text{SO}_4)_3$ ; and (2) an iridescent blue or black sulphide deposit insoluble in water and containing up to 5% of carbon. By modifying the burners an oxidising atmosphere was maintained which reduced the corrosion.

Glass furnaces have been the subject of several investigations particularly from the viewpoint of economic working. The Furnace Committee of the Society of Glass Technology<sup>191</sup> have made suggestions regarding the assessment of the thermal performance of tank furnaces for melting glass and L. Moxon, F. Winks, and B. P. Dudding<sup>192</sup> have reported on the

<sup>186</sup> *J. Inst. Elect. Eng.*, 1944, 91, Part II, 77; B., 1944, I, 346.

<sup>187</sup> *Wärme*, 1943, 66, 169; B., 1945, I, 273.

<sup>188</sup> *Arch. Wärmewirts.*, 1943, 24, 199; *Z. Ver. deut. Ing.*, 1944, 88, 171; B., 1945, I, 201.

<sup>189</sup> *Nature*, 1945, 156, 302.

<sup>190</sup> *Trans. Amer. Soc. Mech. Eng.*, 1945, 67, 279. See also *U.S. Bur. Mines*, 1944, *Tech. Paper* 663; B., 1945, I, 81.

<sup>191</sup> *J. Soc. Glass Tech.*, 1944, 28, 33r; B., 1944, I, 365.

<sup>192</sup> *Ibid.*, 53r; B., 1944, I, 365.



thermal performance of such a furnace fired by coke-oven gas, on the basis of these suggestions. Y. P. Varshney<sup>193</sup> has reviewed annealing, melting, and subsidiary furnaces in the glass industry, frit and muffle furnaces in the enamel industry, and kilns in the pottery industry, and has suggested improvements. F. G. Schwalbe<sup>194</sup> has described refinements and improvements in the design of glass tank furnaces. R. S. Arrandale<sup>195</sup> has discussed the operation and control of glass-melting furnaces and R. G. Abbey<sup>196</sup> the excellent service given by unburnt chrome bricks in the regenerators and superstructures of glass tanks.

A. Dimsdale and M. Francis<sup>197</sup> have described modifications in the structure and operation of pottery ovens which have resulted in considerable reductions in fuel consumption. The Institute of Fuel has held a symposium<sup>198</sup> on the application of underfeed stokers to the firing of industrial furnaces and A. C. Dunningham and B. M. Thornton<sup>199</sup> have discussed mechanical stokers for shell-type boilers. A review of published papers by F. B. Karthauser<sup>200</sup> shows that there is not much reliable information about the performance of shell boilers; the correlation of various tests and operating experiences under the general headings of heat transfer, gas flow, and insulation, however, indicated some directions in which immediate improvements could be made, and others which would repay investigation. M. W. Thring<sup>201</sup> has reviewed critically published information on furnace-port design.

#### ANALYSIS AND TESTING.

The American Society for Testing Materials<sup>202</sup> has published proposed methods of test for the following: expansion pressure of coal during coking, plastic properties of coal by the Davis and the Gieseler types of plastometer, carbonisation pressure of bituminous coal, and expansion properties of coal for use in by-product coke ovens by means of the Bethlehem test oven. A. P. Schachno<sup>203</sup> has discussed the history of the determination of volatile matter in coal and described the standard procedure adopted in various countries; nearly 200 references are cited. R. A. Mott and C. E. Spooner<sup>204</sup> have compared the B.S. and the A.S.T.M. volatile matter determinations in the case of lignites and per-hydrous coals. A rapid method for determining surface moisture in coal has been described by L. D. Schmidt and W. Seymour<sup>205</sup>; it is based on the

<sup>193</sup> *J. Sci. Ind. Res. India*, 1944, **3**, 213; B., 1945, I, 127.

<sup>194</sup> *Glass Ind.*, 1944, **25**, 550, 562; B., 1945, I, 127.

<sup>195</sup> *Ibid.*, 1945, **26**, 19, 75, 128, 177; B., 1945, I, 330.

<sup>196</sup> *Ibid.*, 279; B., 1945, I, 330.

<sup>197</sup> *Trans. Ceram. Soc.*, 1945, **44**, 1; B., 1945, I, 224.

<sup>198</sup> *J. Inst. Fuel*, 1944, **17**, 133; B., 1944, I, 345.

<sup>199</sup> *Ibid.*, 145; B., 1944, I, 345.

<sup>200</sup> *Ibid.*, **18**, 30.

<sup>201</sup> *Brit. Coal Utilisation Res. Assoc. Bull.*, 1945, **9**, 277.

<sup>202</sup> *Proc. Amer. Soc. Test. Mat.*, 1943, **43**, 293—316.

<sup>203</sup> *Trans. All-Union Conf. Anal. Chem.*, 1944, **3**, 143; C., 1945, 14.

<sup>204</sup> *Fuel*, 1945, **24**, 106; B., 1945, I, 319.

<sup>205</sup> *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3811; C., 1945, 165.



idea that the surface moisture is dissolved quickly by solvents such as alcohols, while the internal moisture of the coal remains essentially unaffected. J. Brown<sup>206</sup> has given full details of the apparatus and technique employed in a rapid determination of the potential gas yield and quality during high-temperature carbonisation. H. E. Blayden, J. Gibson, and H. L. Riley with J. Brown, W. Lawson, and J. H. Jones<sup>207</sup> have suggested the use of Caledon Jade Green or a similar dibenzanthrone derivative as a suitable material for standardising coal-assay apparatus. A. Gillet<sup>208</sup> has given a comparative description and an account of critical tests of the methods of Arnn, Gieseler, Foxwell, and Crussard and Gauzelin for determining the fusion characteristics of bituminous coals; he considers the last method to be the best and has suggested certain improvements.

It has hitherto been assumed that during the burning off of the carbonaceous matter in the determination of the ash content of coal or coke, none of the potassium, sodium, calcium, silica, etc. is volatilised; A. H. Edwards and A. O. Pearce<sup>209</sup> have shown, however, that up to 60% of the original sodium or potassium content may be lost when the ash of the fuel is prepared by combustion in a muffle furnace kept at 800°.

<sup>206</sup> *Fuel*, 1945, 24, 38; cf. *C.*, 1945, 14.

<sup>207</sup> *Inst. Fuel War Time Bull.*, 1945, Feb., 128; *C.*, 1945, 105.

<sup>208</sup> *Mem. Assoc. Ing. Liège*, 1943, 144.

<sup>209</sup> *Nature*, 1944, 154, 463.



# GAS, DESTRUCTIVE DISTILLATION, TAR, AND TAR PRODUCTS.

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S. E. WHITEHEAD,<sup>1</sup> in his Presidential address to the Institution of Gas Engineers, drew attention to the fact that between 1921 and 1938, the gas industry increased the amount of coal it processed by 17% but, against this, sold 42% more gas, 30% more coke, and 47% more tar, improvements representing an increase of 15% in thermal efficiency in 17 years. The further developments which have been made during the war have now been illustrated by the publication of more detailed statistical information<sup>2</sup> for that period than has yet appeared. The data in the appended table have been extracted from this, and they show that between 1938 and 1944 there was a notable increase in the supply of gas, and that this was provided mainly by a greater use of purchased coke-oven gas and an increased production of water-gas, the latter reflecting the growing difficulty of obtaining coal.

## FUEL CONSUMPTION AND GAS PRODUCTION.

	1938.	1943.	1944 (provisional).
<i>Consumption.</i>			
Coal, 1000 tons .. ..	19,128	20,740	20,777
Gas oil, 1000 gallons .. ..	32,707	50,390	96,118
<i>Production.</i>			
Coal gas, mill. cu. ft. .. ..	285,003	298,510	296,103
Water-gas .. ..	27,636	40,813	60,125
Other gas .. ..	6,910	8,781	7,661
Coke-oven gas bought .. ..	29,621	46,907	49,081
	<hr/> 349,170 <hr/>	<hr/> 395,011 <hr/>	<hr/> 412,970 <hr/>

During the year there have been a number of publications dealing with the reorganisation and integration of the industry. G. E. Foxwell,<sup>3</sup> in considering the position of the carbonising industry, recommended the development of a greater degree of co-operation between the coke-oven and gas industries, with the joint supply of gas through regional grids under a Central Carbonisation Board similar to the Central Electricity

<sup>1</sup> *Inst. Gas Eng.*, 1945, *Comm.* 277; *Gas J.*, 1945, 245, 754; *Gas World*, 1945, 122, 568.

<sup>2</sup> *Gas Times*, 1945, 43, 218.

<sup>3</sup> *Gas World*, 1945, 122. *Coking Sect.*, 23.



Board. J. Mitchell<sup>4</sup> also advocated a Central Board which was visualised as controlling the activities of seven Regional Boards. This author criticised the industry for being slow in the development of promotional and two-part tariffs and for not co-ordinating policy and design in appliance manufacture.

In June, 1944, the Heyworth Committee was set up by the Minister of Fuel and Power to review the structure of the industry and to recommend methods whereby gas supplies might be improved and cheapened. The Committee issued its Report towards the end of 1945.<sup>5</sup> This proposes that the industry should be nationalised, with control by Regional Boards, each of which would consist of a Chairman and six Directors, to be appointed by the Minister. Ten Regions are suggested for England, Scotland, and Wales, the boundaries indicated tentatively being intended to bring major concentrations of population within single Regions, to have sufficient resources to support the type of administration proposed, and to ensure that each Region includes "one or more units with a tradition and present reputation for high efficiency." The Boards would be directly and severally responsible to the Minister. They would undertake such measures of integration and technical development within the Regions as would promote the maximum use of gas, and would be responsible for the maintenance of the statutory requirements as regards gas quality. The administrative machinery for gas examination and testing should be revised and transferred to the Ministry of Fuel and Power. It is also proposed that the Regional Boards should be empowered to establish a fund by means of a levy on gas sales to extend the scope of centralised research such as is carried out by the Gas Research Board, but that they should themselves devote effort to technical research and development. This Report is now being considered by the Government.

With the cessation of hostilities, restrictions on the publication of technical information have been lifted, and papers previously withheld are appearing. The Institution of Gas Engineers has resumed its Autumn Research Meetings.

#### CARBONISATION.

Concern is frequently expressed regarding the coal reserves of Great Britain, it being increasingly appreciated that, many of the best seams having been extensively worked, it is incumbent on the consumer to use efficiently the most suitable coal for his purpose and perhaps to accept coals of poorer quality than those to which he may have become accustomed. In this connexion, the Reports of the Coal Survey organisation of the Fuel Research Board have proved to be of great value, although as yet they have been limited to quantitative information on the nature of our coal seams.

<sup>4</sup> "The British Gas Industry, Present and Future"; *Fabian Publ. Res. Ser.*, No. 103, 1945.

<sup>5</sup> H.M.S.O., *Cmd.* 6699, 1945.



During the year Reports with a wider aspect have been prepared by the Regional Survey Committees and issued<sup>6</sup> by the Ministry of Fuel and Power; they have combined economic and statistical information with the technical data of the older Survey reports. A. Parker<sup>7</sup> has indicated that similar investigations are to be undertaken by the Coal Survey organisation, and eventually complete quantitative and qualitative information will be available regarding our coal reserves. Preliminary estimates suggest that within 100 years there is not likely to be a shortage of the varieties of coal suitable for gas-making by carbonisation. It appears, on the other hand, that the special Durham coals which provide the best metallurgical cokes may approach exhaustion within 50—70 years, although it is stressed that good blast-furnace coke can be, and already is being, made from coals of lower rank.

A conference arranged by the Institute of Fuel<sup>8</sup> on the preparation and utilisation of coal gave an opportunity for a frank discussion between coal producers and representatives of the major consuming industries. The losses incurred in coal preparation were given and it was plain that unnecessary and avoidable cleaning was not in the best interests of coal conservation. H. C. Applebee, H. H. Thomas, and J. A. Tomlinson stated the needs of the gas industry for carbonisation in various types of plant, and advocated that gas-making coals should be reserved and not used indiscriminately.

Further theoretical studies in carbonisation have been made by H. E. Blayden, J. Gibson, and H. L. Riley,<sup>9</sup> using the methods of X-ray crystallography. When coals and other complex carbonaceous materials are heat-treated, the *c* dimension of the carbon crystallites formed reaches in some cases a maximum when the temperature of treatment is about 550°. The maximum is more pronounced with strongly caking coals. The phenomenon is believed to be due to the stacking of lamellar aromatic molecules, which are not decomposed or volatilised at temperatures below 600°, and which have been shown to be extracted when coals are treated with pyridine. Certain synthetic dyes, *e.g.*, dibenzanthrone, which have a condensed aromatic nuclear structure, exhibit similar behaviour, in contrast with derivatives of cellulose or lignin. It is concluded that coking is associated with the presence in the coal of molecules with a relatively flat aromatic structure, which retain mobility up to 400—600°. The presence of such molecules enables fluid films to be formed and agglutination to take place.

W. Hirst and J. Sandor<sup>10</sup> have studied the mechanism of electrical conductivity in carbonised coals, and have related the magnitude of the

<sup>6</sup> H.M.S.O., 1945.

<sup>7</sup> *J. Inst. Fuel*, 1945, **18**, 158.

<sup>8</sup> *Ibid.*, 93.

<sup>9</sup> *Inst. Fuel War-Time Bull.*, 1945, *Feb.*, 117; *B.*, 1945, **I**, 144.

<sup>10</sup> *Coal Res.*, 1945, **3**, 96.



energy barrier opposing the movement of electrons in the cokes to the nature of the original coal and to the temperature of carbonisation.

G. C. Soth and C. C. Russell<sup>11</sup> have investigated the development of swelling pressures on carbonisation, and attribute it to the resistance offered to the volatile matter by the plastic coal. They consider that experiments with a small sample enable the pressure developed by a coal during commercial-scale carbonisation to be predicted. As a result of an examination of 19 American bituminous coals, R. E. Brewer<sup>12</sup> has correlated the fluidity with the rank of the coal, indicating that allowances have to be made for the disturbing influences of such constituents as anthraxylon, mineral matter, and oxygen. The same author<sup>13</sup> has published a comprehensive review of the plastic and swelling properties of bituminous coals.

From experiments on the source of the methane produced on carbonisation, C. R. Kinney<sup>14</sup> has concluded that the percentage yield under fixed carbonisation conditions is constant for many bituminous coals. Yields from peat and lignin are larger than from cellulose, and it is suggested that coals are more probably derived from lignin than from cellulose.

A number of papers has appeared devoted to questions of immediate practical significance in coal carbonisation. J. G. King<sup>15</sup> has discussed the effect of carbonising coals, such as house coals, which are of smaller caking power than those which would normally be chosen. Decreasing caking power is accompanied by an increase in moisture content, by a decrease in calorific value and thermal yield in the gas, and, of course, by increases in the friability of the coke and in the proportion of breeze produced. Some house coals are so feebly caking that they could be used only when sized or blended with a caking coal. On the other hand, there is a gain in the reactivity of the coke. Experiments on carbonisation in various types of plant are quoted; intermittent vertical chambers appear to be less dependent than horizontal or continuous vertical retorts on the caking power of the coal supplied. It is pointed out that house coals differ materially in caking properties according to locality; those from South Yorkshire, for example, which have distinct caking properties, could be carbonised instead of gas coals with less sacrifice of gas yield, coke strength, etc. than could Midland house coals.

J. G. King, D. MacDougall, and H. Bardgett<sup>16</sup> have commenced a study of the influence of free space in the retort during carbonisation. Horizontal retorts were used, and as the free space was increased, the thermal yield of gas per ton increased also. At first the yield of tar

<sup>11</sup> *Trans. Amer. Inst. Min. Met. Eng.*, 1944, 157, 281; cf. C., 1944, 68.

<sup>12</sup> *Ind. Eng. Chem.*, 1944, 36, 1165; B., 1945, I, 118.

<sup>13</sup> *U.S. Bur. Mines*, 1942, *Bull.* 445; *Chem. Abs.*, 1945, 601.

<sup>14</sup> *Fuel*, 1945, 24, 16; B., 1945, I, 118.

<sup>15</sup> *J. Inst. Fuel*, 1945, 18, 148.

<sup>16</sup> *Gas J.*, 1945, 246, 259, 263; B., 1945, I, 320.



rose with that of gas, but with the smallest charges it decreased, with a rise in its free carbon content. The effect of free space was more pronounced when it was obtained by using a shallow rather than a short charge.

In the United States the blending of anthracite fines with coking coal has attracted attention in the manufacture of metallurgical coke. W. Seymour and L. D. Schmidt<sup>17</sup> consider that in many plants 3—5% of low-volatile anthracite fines could be used instead of a similar proportion of coking coal without seriously affecting the quality of the resulting coke. J. D. Clendenden, E. M. Barclay, and C. C. Wright<sup>18</sup> have examined the size-distribution, specific gravity, and volatile matter content of anthracite fines in relation to their suitability for blending. Coarser grades give cokes suitable for foundry work, while blast-furnace coke results from the admixture of fine grades with the charge for carbonisation. The addition of anthracite of a low specific gravity favours the production of a strong coke.

War-time experiments on the production, at gas works, with relatively small modifications in standard operating procedures, of coke of sufficient reactivity for use in mobile producers have been described by H. D. Greenwood and J. G. King, and by T. F. E. Rhead and E. T. Pickering.<sup>19</sup> The former authors showed that sufficiently reactive cokes could be prepared from coals of moderate caking power in continuous vertical retorts at temperatures about 50° below, and throughputs about 15—20% above, normal. The calorific value of the gas made during the carbonisation was not materially affected by these modifications, but the yield per ton was reduced. Test runs with the mobile producer brought out the importance of sizing the coke. Rhead and Pickering investigated the alkali-activation of cokes prepared in the manner described. The sized product was sprayed at 120° with an 18% aqueous solution of sodium carbonate, and then dried.

Various aspects of routine inspection, maintenance, and control of retort houses have been discussed by P. E. Gallaher,<sup>20</sup> C. E. Deas,<sup>21</sup> and R. N. Hateley,<sup>22</sup> whilst W. Lenhardt<sup>23</sup> has described fuel economy in carbonisation by the utilisation of waste heat and the reduction of radiation and conduction losses.

In normal carbonisation, the volatile products pass through the coke and the hottest part of the retort, and the resulting cracking of tar vapours reduces the yield of condensable products, gives rise to scurf, and lowers the reactivity of the coke. In the Still oven these effects are minimised by withdrawing the gases and vapours through pipes inserted

<sup>17</sup> *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3808; B., 1945, I, 248.

<sup>18</sup> *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 405; B., 1946, I, 158.

<sup>19</sup> *Inst. Gas Eng.*, 1945, *Comm.* 281; B., 1945, I, 248.

<sup>20</sup> *Gas J.*, 1945, **245**, 83; B., 1945, I, 90.

<sup>21</sup> *Ibid.*, 53; B., 1945, I, 90.

<sup>22</sup> *Ibid.*, 500; B., 1945, I, 176.

<sup>23</sup> *Oel u. Kohle*, 1943, **39**, 159; B., 1945, I, 284.



into the centre of the charge, and T. Biddulph-Smith<sup>24</sup> has found that secondary decompositions can be still further suppressed if steps are taken to prevent the formation of impermeable plastic layers. He claims high yields of liquid products and a coke of high reactivity, although the gas yield was low; e.g., on an experimental scale only 3000 cu. ft. per ton, calorific value 700—800 B.Th.U. per cu. ft., were obtained.

### PURIFICATION.

In continuous methods of ammonia recovery from gasworks liquor by means of the conventional lime treatment and steam-distillation, control of the pH value of the ammonia solution is of importance since it determines the ratio of the concentration of vapour to liquid phase ammonia. Patents taken out by the Gas Light & Coke Co., Ltd., with W. G. Adam, D. G. Murdoch, and W. E. Golding<sup>25</sup> have described a method of automatic control in which instruments governed by the pH value operate the lime and steam delivery valves. W. Mottram<sup>26</sup> has described a method of producing liquor of a predetermined specific gravity in which a float valve chamber is coupled to the last washer compartment and determines the rate of water supply.

W. O. Renkin<sup>27</sup> has given a method for the production of improved grades of ammonium chloride from weak liquors, the first step consisting of a rapid concentration of the liquor while it is flowing at a sufficient speed to prevent the deposition of tar and suspended solids. After the removal of the latter, by filtration, the liquor is dehydrated by spraying it into a heated gas stream from which the ammonium chloride is precipitated in the form of a dry powder. This is then purified by redissolution, treatment with active carbon, and a second precipitation by a further flash treatment.

An account of developments in the purification plant at Hinckley Gas Works has been given by A. B. Britton.<sup>28</sup> It includes electrostatic tar precipitation at 160—170° F., before liquor condensation, and a second feature is the avoidance of cyanide oxidation by delaying the admission of air for purification until the entry of gas into the oxide boxes. An ammonium sulphate plant was successfully converted for the production of concentrated liquor containing more than 22% of  $\text{NH}_3$ .

G. U. Hopton and R. H. Griffith<sup>29</sup> have made an important contribution to the chemistry of the absorption of hydrogen sulphide by iron oxide. They find that "of the seven known forms of ferric oxide, all except  $\beta\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  react completely with hydrogen sulphide to give the sulphide  $\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O}$ . This sulphide hydrate is readily oxidised (with air) to

<sup>24</sup> *Gas J.*, 1945, 246, 56, 59, 65, 69; *B.*, 1945, I, 283.

<sup>25</sup> B.P. 570,395 and 570,421; *B.*, 1945, I, 350.

<sup>26</sup> B.P. 570,056; *B.*, 1945, I, 354.

<sup>27</sup> U.S.P. 2,189,083; *B.*, 1945, I, 146.

<sup>28</sup> *Gas J.*, 1945, 245, 436; *Gas World*, 1945, 122, 224; *B.*, 1945, I, 146.

<sup>29</sup> *Inst. Gas Eng.*, 1945, *Comm.* 288; *B.*, 1946, I, 124.



$\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  if conditions of pH, temperature, and moisture are satisfactory. Under acid conditions or at temperatures above  $50^\circ \text{C}$ . the sulphide decomposes into  $\text{FeS}_2$  and a strongly magnetic sulphide  $\text{Fe}_3\text{S}_4$ . Oxidation of these two sulphides takes place with very much more difficulty than does that of  $\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O}$  and the resulting oxide is not active for the absorption of more hydrogen sulphide. The best performance for removal of hydrogen sulphide from fuel gases is given by  $\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  while  $\gamma$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is slightly less satisfactory. The inferior results with anhydrous oxides are due in some cases to the difficulty of preparing them in a sufficiently porous state, partly because they easily give an anhydrous sulphide, difficult to oxidise, and partly owing to the fact that their reaction with hydrogen sulphide is subject to an induction period, so that they are not suitable for the removal of traces of hydrogen sulphide. Oxidation of  $\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O}$  under proper conditions always gives  $\alpha$ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and it is possible for improvement in the performance of less satisfactory purifying materials to take place by this means after one or two cycles in use."

Hopton and Griffith state that chemically precipitated forms of iron oxide can be prepared in a state which is highly satisfactory as regards both pore structure and reactivity, and a patent of Hopton and the Gas Light & Coke Co.<sup>30</sup> describes the use in tower purifiers of an absorption material produced from commercial ferrous sulphate and slaked lime. These materials were mixed, pasted with water, shaped into pellets, and air-dried, sometimes with the addition of a cement. The pellets were fed into the top of the tower countercurrent to the gas stream and removed at the base for revivification. The tower operated at 15 times the space velocity of normal oxide boxes and the back pressure thrown was only 2 in. water gauge.

R. J. S. Thompson<sup>31</sup> has surveyed the principal existing methods for the purification of coal gas to statutory standards: he favours the use of oxide, particularly in tower scrubbers, and visualised future developments in this practice as being towards mechanical control and mobile rather than static forms of oxide utilisation.

H. G. Pyke<sup>32</sup> has made investigations of the absorption and oxidation of hydrogen sulphide which indicate that the activity of a natural Australian oxide was dependent on the presence of amorphous ferric hydrate, and was best used under slightly alkaline conditions at  $29$ – $32^\circ$  and containing about 15% of moisture. He alleges that the presence of manganese dioxide improves the initial activity but the effect disappears after two foulings. The production of an extremely finely-divided ferric oxide is claimed by precipitation from a ferric sulphate solution on the addition of ammonia in a 6–12% excess; subsequent air-blowing produces

<sup>30</sup> B.P. 567,231; B., 1945, I, 146.

<sup>31</sup> *Gas World*, 1945, 122, *Coking Sect.*, 41; B., 1945, I, 284.

<sup>32</sup> *J. Proc. Austral. Chem. Inst.*, 1945, 12, 16; B., 1945, I, 176.



a stable and easily filterable oxide. G. Campen<sup>33</sup> has explained the formation and nature of the insoluble cyanide complex Prussian Blue found in spent oxides from gas purification.

C. W. Cooper and H. Waddle<sup>34</sup> have given an account of the purification of the sourest natural gas yet encountered in the U.S.A., containing 4450 grains of hydrogen sulphide per 100 cu. ft. 96.7% of the hydrogen sulphide is removed in a Girdler amine plant. A. R. Powell and the Koppers Co.<sup>35</sup> have patented a method of removing hydrogen sulphide and carbon dioxide from gases by means of solutions containing carbonate and bicarbonate ions; the washing solution is circulated after regeneration partly with steam at 50—60° and reduced pressure, and partly by boiling at 130° under pressure, this system being regulated to preserve the most suitable  $\text{CO}_3^{''}:\text{HCO}_3'$  ratio.

The various methods which have been developed for the removal of organic sulphur from town gas are effective in varying degrees with different individual compounds, and their best application clearly depends on a knowledge of the variations which are known to exist in the amount and nature of the compounds present. To provide this information, J. W. Wood and E. W. Claydon<sup>36</sup> have embarked upon a survey of typical town gases, and a report has been published giving the first results and some preliminary conclusions. Tests are described on several unwashed gases from horizontal and vertical retorts, carburetted water-gases, blue water-gases, and producer gases, which record the quantities of mercaptans, thiophen, carbon disulphide, and volatile sulphur compounds in each. The total organic sulphur concentrations of the gases examined ranged from about 10 to 50 grains per 100 cu. ft. and values of 20—35 grains were common. Gas from horizontal retorts contained on the average more sulphur than gas from vertical retorts, although there was little difference when the gases had been brought to the same calorific value. The type of vertical retort appeared to be of minor consequence. In coal gas the predominating sulphur compound was found to be carbon disulphide, which frequently accounts for half the total. Carburetted water-gas contained much less sulphur than average coal gas, and, as with blue water-gas and producer gas, its predominating constituent was carbon oxysulphide.

A. Key and A. H. Eastwood<sup>37</sup> have given a detailed report of the past six years' work on the catalytic conversion of sulphur compounds carried out at the University of Leeds. The high degree of purity required in synthesis gas for methane production occasioned the research, but it was later extended to the purification of coal gas. Early experiments

<sup>33</sup> *Gas- u. Wasserfach*, 1943, 86, 93; B., 1945, I, 119.

<sup>34</sup> *Gas*, 1945, 21, No. 7, 31.

<sup>35</sup> U.S.P. 2,318,522—3; B., 1945, I, 120.

<sup>36</sup> 48th Rept., Joint Res. Cttee., Gas Res. Board and Leeds Univ., Gas Res. Board, Publ. GRB. 17, 1945; B., 1946, I, 124.

<sup>37</sup> *Ibid.*, Publ. GRB. 14, 1945.



showed that certain metallic sulphides possessed considerable activity for the conversion of organic sulphur compounds into hydrogen sulphide at temperatures as low as  $250^{\circ}\text{C.}$ , but investigations on their failure to effect complete conversion indicated the attainment of an equilibrium involving organic sulphur and hydrogen sulphide. Results depended on the relative extent to which the two reactions  $\text{COS} + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{S}$  and  $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$  were catalysed. It was found that a catalyst which preferentially accelerated the hydrolysis reaction would at  $250^{\circ}$  give the greatest conversion of organic sulphur. A supported copper-chromium catalyst was developed capable of reducing the organic sulphur in water-gas and synthesis gas to 0.2 grain per 100 cu. ft. at high space velocity. This degree of reduction was insufficient to meet the standards required for synthesis work, but it was found that by giving three treatments with intermediate removal of hydrogen sulphide such gases could be obtained with less than 0.002 grain of sulphur per 100 cu. ft. When this catalyst was used with coal gas, however, at a temperature below  $400^{\circ}$ , it was rapidly rendered inactive due to the gas containing certain unsaturated compounds of the acetylene type. It was established that a pretreatment of the coal gas with a hydrogenating nickel or molybdenum sulphide catalyst at  $300^{\circ}$  destroyed the acetylenic compounds and prevented the subsequent poisoning of the copper-chromium catalyst. Then it was found possible to convert most of the organic sulphur compounds with the exception of thiophen, which, as in other catalytic processes, passed through with little change.

L. N. Boyer<sup>38</sup> has patented a desulphurisation process based on the treatment of gases with charcoal impregnated with potassium carbonate or hydroxide and used at  $300\text{--}450^{\circ}$ . A long life is claimed for the catalyst, which converts the mercaptans and some additional sulphur compounds into hydrogen sulphide, which it then absorbs. It is regenerated periodically by superheated steam, although in practice this can be avoided by adding 10—20% of steam to the gas prior to treatment. An example cited shows that a reduction from 0.14% of total sulphur to 0.04% could be achieved on a single pass at about  $400^{\circ}$  and to 0.006% at  $450^{\circ}$ .

A mechanical method of removing entrained solids from gases down to a particle size dimension of 0.005 mm., by passing through tubes of first gradually decreasing and then increasing cross-section, has been patented by L. Silver and the Gas Light & Coke Co.<sup>39</sup>

### BENZOLE, TAR, AND TAR PRODUCTS.

The tar distillation industry was selected as the subject for this year's Stevens Memorial Lecture, and in making this address W. G. Adam<sup>40</sup> gave a detailed survey of the history and present practice of the industry.

<sup>38</sup> U.S.P. 2,379,654.

<sup>39</sup> B.P. 569,866; B., 1945, I, 318.

<sup>40</sup> *Jun. Inst. Eng. J. and Rec. of Trans.*, 1945, 55, 325.



It may be noted that the author considered that the annual production of crude benzole (90—100,000,000 gallons) was now approaching the limit unless more coal was carbonised in the future than the pre-war average of 40,000,000 tons per year. As an example of the changes which have taken place in the industry, he cited the fact that whereas in the early days benzole was solely obtained from tar, now it is the gas which yields by far the greater amount.

J. S. Sach<sup>41</sup> has given an account of processes and trends of development in a new edition of "Coal Tar Fuels," and the annual review of production figures, with prices of raw materials and by-products, is included in the Report of the Association of Tar Distillers for 1944.<sup>42</sup> The Minister of Fuel and Power has stated<sup>43</sup> that the use of coal-tar oil as a substitute for imported liquid fuel has expanded from less than 100,000 to more than 600,000 tons per annum during the war period.

An outline of the theory of benzole scrubbing with oils, and conditions for optimum yields, was given by J. Pluckthün<sup>44</sup> together with information on recent Continental practice. In this country further details have been published<sup>45</sup> of the Beckton plant of the Gas Light & Coke Co., including the methods used to remove impurities from the benzole down to specification standards, *e.g.*, thiophen, by washing with sulphuric acid, and carbon disulphide, by close fractionation and concentration in the forerunnings. The inhibition of gum formation is effected by the addition of 0.04% of cresylic acid in place of the previous exhaustive acid-washing treatment.

G. W. Robson<sup>46</sup> has given some details of the 400,000 cu. ft. per day active carbon plant at Morpeth, and there has been a discussion<sup>47</sup> of the respective merits of the active carbon and wash-oil processes.

Appleby-Frodingham Steel Co., and H. P. Stephenson<sup>48</sup> have proposed a process for the acid refining of benzole by which it is claimed that the sulphuric acid consumption, refining losses, and plant corrosion are reduced, the process depending on washing with acid after fractionating the crude spirit.

E. J. Dickinson<sup>49</sup> has investigated the properties of road tars prepared from three representative horizontal- and vertical-retort and coke-oven tars. The tars were divided into five fractions by distillation and solvents. Measurements of the mean molecular weight and C/H ratio of these fractions support the theory that high-temperature tar is formed by a cracking process and contains a range of predominantly aromatic molecules

<sup>41</sup> "Coal Tar Fuels," 1944, Association of Tar Distillers, 140 pp.

<sup>42</sup> *Gas Times News Bull.*, 21 April, 1945, 10; *Chem. Trade J.*, 1945, 116, 396.

<sup>43</sup> *Coll. Guard.*, 1945, 170, 423.

<sup>44</sup> *Oel u. Kohle*, 1943, 39, 91; *B.*, 1945, I, 10.

<sup>45</sup> W. G. Adam, *loc. cit.*

<sup>46</sup> *Gas World*, 1945, 123, 399.

<sup>47</sup> *Gas Times*, 1944, 41, 227; 1945, 42, 12.

<sup>48</sup> B.P. 589,003; *B.*, 1945, I, 251.

<sup>49</sup> *J.S.C.I.*, 1945, 64, 121; *B.*, 1945, I, 210.



in which the C/H ratio increases with molecular weight. The cryoscopic behaviour in benzene of the fractions of higher molecular weight, and the viscosity of their dispersions in tar oils, indicate that these substances are present in an associated state, the degree of association increasing with molecular weight. Examination of the tars in the electron microscope showed a particulate structure of colloidal dimensions. It is suggested that tar is an associated colloid in which the units are composed of a core of hydrocarbons of high molecular weight surrounded by a solvation layer of hydrocarbon molecules of lower molecular weight. These micelle units are dispersed in a continuous oily medium and there is no abrupt discontinuity of phase between this medium and the nuclei of the micelles.

D. W. Milner<sup>50</sup> has stated that while the use of phenol as an antiseptic was declining because of the introduction of more efficient and less toxic allied products, the demand for phenol in the production of bakelite and other plastics was now such that it must be synthesised. Similarly, new developments in the textile and drug industries had created a much greater demand for pyridine, picoline, and other derivatives. He visualised increased interest in methods of sulphur recovery, and referred to the development of the ammonium polysulphide (Yorkshire Tar Distillers') process for the recovery of carbon disulphide from crude benzole forerunnings, and its growing use as a solvent, rubber accelerator, and base for carbon tetrachloride manufacture. The author, in thus pointing out the growing demand for organic chemicals, emphasised that there is a large potential source of them in coal tar.

The probability that the time might soon arrive when coal would be processed mainly for its by-products was forecast by J. I. Jones<sup>51</sup> in a survey of the prospects of coal, petroleum, or agricultural products meeting the future needs of the plastics industry; W. E. de B. Diamond<sup>52</sup> has indicated that 95% of the plastics made in Britain are derived from by-products of carbonisation, and has illustrated the uses which the gas industry can make of plastic articles and materials. R. M. Bridgwater<sup>53</sup> has summarised the results of recent British research on the development of petroleum substitutes by the hydrogenation of tars and tar products.

A review<sup>54</sup> of phenol recovery from liquors discussed the Triphos, Phenosolvan, and Koppers processes, and made a brief reference to the method developed by the Wiederlausitzer Kohlenwerke, in which the oil used in benzole recovery is applied to dephenolation before the impurities are removed by fractionation. These techniques were compared from the point of view of steam, power, cooling water, and solvent

<sup>50</sup> *J. Inst. Fuel*, 1945, **18**, 80; *Gas World*, 1945, **121**, 626; *Gas J.*, 1945, **245**, 154, 157; *B.*, 1945, **I**, 144.

<sup>51</sup> *Brit. Plastics*, 1945, **17**, 358.

<sup>52</sup> *Inst. Gas Eng.*, 1945, *Comm.* 282; *B.*, 1945, **I**, 249.

<sup>53</sup> *Petroleum*, 1945, **8**, 68.

<sup>54</sup> *Ind. Chem.*, 1945, **21**, 405, 495.



consumptions. Further Continental practice was reviewed by F. Rosendahl.<sup>55</sup> A. N. Baskirov and I. M. Vener<sup>56</sup> have given an account of both vapour- and liquid-phase methods for the production of phenol from phenol-cresol tar fractions, using an alkali-activated iron obtained from bog ore and reduced with hydrogen. H. G. Druckamer, G. G. Brown, and R. R. White<sup>57</sup> have published vapour-liquid equilibrium data at atmospheric pressure for mixtures of toluene, methylcyclohexane, paraffin hydrocarbons, and phenol.

The South Metropolitan Gas Co., H. Stanier, and J. E. Davis<sup>58</sup> have patented a method for the production of toluene by pyrolysis of xylene or xylene-rich fractions at 600–1000° in the presence of hydrogen or hydrogen-rich gases. G. R. Lake<sup>59</sup> has employed azeotropic methods to separate toluene from paraffins and has reported a 95% recovery by using mixtures of methyl ethyl ketone and water in a 50-plate column with a 2 : 1 reflux ratio.

Details have been given<sup>60</sup> of the performance of two Simon-Carves electrostatic detarrers, each of a throughput of 4,000,000 cu. ft. per day, installed at St. Helens Gas Works. The coal gas treated contained 90–135 grains of tar per 100 cu. ft. and a removal efficiency of 99.4% was reported with a consumption of 8.2 kw.-hrs. per million cu. ft. of gas.

#### GASIFICATION.

The interplay of reactions in a column of burning fuel is an inexhaustible source of interest, and an account of a further research has now been published. In this instance, J. Hiles and R. A. Mott<sup>61</sup> have paid special attention to the influence of fuel size and reactivity. In common with previous workers they found that the main product in the air entry zone was carbon dioxide, which, although it never reached the theoretical concentration, represented an increasing proportion of the carbon supplied (up to 90%) as the size of the fuel increased and its reactivity decreased. Some of the carbon dioxide was thought to result from the combustion of primarily formed carbon monoxide, which burnt rapidly as long as an appreciable concentration of oxygen remained. The consumption of the oxygen had not, however, to be complete before carbon monoxide survived and before carbon dioxide was reduced by the carbon. This effect was indeed sufficient for the authors to conclude that a distinction between primary and secondary reaction zones is unjustified. The maximum temperature of the fuel bed occurred at the point of maximum carbon dioxide concentration and was highest for fairly large sizes of coke. By control of the size conditions in the bed could be varied over a wide range.

<sup>55</sup> *Gas- u. Wasserfach*, 1943, **86**, 424; B., 1945, I, 10.

<sup>56</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1944, 48; B., 1945, I, 55.

<sup>57</sup> *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 555; A., 1946, I, 43.

<sup>58</sup> B.P. 569,035; B., 1945, I, 251.

<sup>59</sup> *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 327; B., 1945, I, 352.

<sup>60</sup> *Gas J.*, 1945, **245**, 371.

<sup>61</sup> *Fuel*, 1944, **23**, 154; B., 1945, I, 55.



Inasmuch as the maximum temperatures developed in fuel beds are much lower than would theoretically be obtained by complete combustion to carbon dioxide, support is derived for the view just outlined. Temperatures depend also, however, on the transport of heat by radiation and conduction in the bed and these aspects have been examined by Z. F. Tschuchanov,<sup>62</sup> who considers the bed to be made up of a series of receiving and radiating screens each corresponding with a layer of fuel particles.

B. R. Warner<sup>63</sup> gives new experimental proof for the existence of isotherms and saturation pressures in the reaction between carbon and steam. The form of these isotherms suggests the adsorption of a uni-molecular layer on the carbon surface and on this hypothesis the author explains an observed increase of the rate of the steam reaction with pressure.

J. G. King<sup>64</sup> has given several heat balances for producers, water-gas and complete gasification plants in a contribution on the thermal aspects of British and foreign practice in the gasification of coal. Comparisons are made between processes where heating is by the recirculation of hot gases, those using externally heated reaction chambers, processes using enriched air and oxygen, and high-pressure processes. Consideration is also given to enrichment by methane synthesis.

A modern producer-gas plant for the gasification of bituminous coal, built by the Power Gas Corporation, Ltd., has been described by P. M. K. Embling.<sup>65</sup> The plant is designed for the production of cleaned cold gas and includes three generators, with special feed hoppers to give a fuel bed of constant depth without size segregation. Gas treatment consists of washing successively with hot water, tar, and cold water, followed by dry filtration. Hydrogen sulphide is removed, if desired, and the gas is then ready for transmission to the point of consumption. From coal containing 36% of volatile matter, average thermal yields are: cold gas 73%, tar 12%. G. Dougill<sup>66</sup> has given an account of experience in the cleaning of the producer gas used to fire the coke ovens at the Beckton works of the Gas Light & Coke Co. The gas, after being washed with estuary water, contains ash, tar, and sodium chloride, the latter to the extent of about 4 grains per 100 cu. ft. These were then removed by an electrostatic tar precipitator, but the deposit had such a consistency that it built up on the electrodes and eventually caused short-circuiting. The difficulty was overcome by evaporating a tar fraction into the gas (1.5 gallons per million cu. ft.) which would condense to a fog on the sodium chloride and other nuclei, rendering the deposit

<sup>62</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **44**, 269; B., 1945, I, 175.

<sup>63</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1306; B., 1945, I, 55.

<sup>64</sup> *Gas World*, 1945, **122**, 220; *Gas J.*, 1945, **245**, 342.

<sup>65</sup> *J. Inst. Fuel*, 1945, **18**, 114; B., 1945, I, 209.

<sup>66</sup> *Inst. Chem. Eng. and Chem. Eng. Group [Soc. Chem. Ind.]*, 1945, *Advance copy*; B., 1945, I, 50.



sufficiently fluid to run off the electrodes and collect in the heated base of the precipitator.

Interest in underground gasification continues. Z. F. Tschuchanov<sup>67</sup> has discussed the conditions which control the temperature during the combustion of layers of coke or virgin coal, and concluded that under some circumstances heat losses may be so high as to lower the combustion temperature and make the gasification inefficient. L. J. Jolley and N. Booth<sup>68</sup> have reviewed the published information on the development in Russia of underground gasification, and include a bibliography of more than one hundred references.

Two reports have appeared on the catalytic synthesis of methane from carbon monoxide and hydrogen, one, by F. J. Dent, L. A. Moignard, A. H. Eastwood, W. H. Blackburn, and D. Hebden,<sup>69</sup> which describes a research carried out during the war at the University of Leeds, and the other, by N. Booth, E. T. Wilkins, L. J. Jolley, and J. A. Tebboth,<sup>70</sup> a parallel investigation made at the Fuel Research Station. The aim was to develop the synthesis for the production of methane for use as an enricher for town gas or as a fuel, the reaction being carried out either at atmospheric pressure with normal water-gas or under pressure with a hydrogen-rich gas such as can be obtained by pressure gasification. Nickel catalysts were found to be the most suitable, and the addition of promoters, sometimes in considerable proportions, was beneficial for the minimisation of the deposition of carbon on the catalyst and loss of activity during exposure to the high temperatures liable to be developed by the synthesis reaction. Methods of controlling the temperature of the catalyst surface were a major consideration of the investigations, and amongst those tried were recirculation of the reaction gases, and the distribution of the gas so that it did not all impinge on the catalyst in one part of the catalyst tube or compartment. Recirculation had an added advantage in that it offered a means of transporting the reaction heat away from the catalyst vessel. The addition of steam was found to be useful in reducing carbon deposition, and, indeed, was necessary when using water-gas, which otherwise gave rise to an unfavourable equilibrium position on account of its high proportion of carbon monoxide. Determinations of the equilibria concerned were made, so that the correct amount of steam to add could be calculated, and it was found that the position of equilibria involving carbon as established over catalysts did not correspond with the separation of the carbon as graphite. It appeared that the equilibria were determined by carbon entering the catalyst as a solid solution. Tests were developed for assessing the relative values of catalysts, the properties examined under standard

<sup>67</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 27, 203; B., 1945, I, 377.

<sup>68</sup> *Fuel*, 1945, 24, 31, 73; B., 1945, I, 284.

<sup>69</sup> 49th Rept., Joint Res. Commee., Gas Res. Board and Univ. of Leeds; Gas Res. Board, 1945, Publ. G.R.B. 20.

<sup>70</sup> Gas Res. Board, 1945, Publ. G.R.B. 21.



conditions being the tendency for the deposition of carbon, the loss of activity on heating, and the capacity to absorb sulphur before poisoning.

Sir Alfred Egerton has conducted an extensive investigation of the possibilities of liquid methane as a fuel for internal-combustion engines, and with M. Pearce<sup>71</sup> has published a full account of it. It is pointed out that methane has several attractive features, which include a remarkable freedom from detonation. Its disadvantages are all connected with the fact that it has to be stored as a cold boiling liquid, and there is, therefore, loss by evaporation. Much of the experimental work has been concerned with reducing this evaporation, and it is noteworthy that in a recent road trial, several of which are described, the evaporation loss was only 2.5% of the methane supplied in the case of a single-decker omnibus working for 15 hours per day. Details of storage tanks and methods of filling them are given as well as of the sources and the processes of liquefaction of methane.

#### GASEOUS COMBUSTION.

W. T. David,<sup>72</sup> continuing his investigations of the abnormalities of flame gases, has given additional evidence in support of the theory that hot gases formed by combustion differ from gases normally heated by possessing a latent energy, which is considered to be due to the formation of molecules of abnormal structure, and which is not readily dissipated. These abnormal molecules, it is reported, are less in evidence in the combustion of hydrogen than with carbon monoxide, and their formation is restricted by increase of pressure. It is suggested that the efficiency of certain flame gases for particular industrial processes may be due partly to the release of this additional latent energy when suitable surfaces are present. The same author, with J. Mann and F. R. Mobbs,<sup>73</sup> has found that when a flame has passed through a homogeneous inflammable mixture, the gases left behind, which are normally luminous, attain an equilibrium, but the measurement of their temperatures is difficult on account of the varying influences exerted on the recombination of dissociated molecules by thermometric wires of different materials.

G. Damköhler and R. Edse<sup>74</sup> have published methods for simplifying the many equations concerned in the calculation of equilibrium conditions in gas mixtures formed by the combustion of hydrocarbons.

J. E. Garside, J. S. Forsyth, and D. T. A. Townend<sup>75</sup> have given an account of further investigations into the ignition velocity and stability of burner flames. In a discussion of the measurement of flame speed a refinement of Gouy's method is described, in which the true surface of the inner cone is used, rather than that of an assumed equivalent

<sup>71</sup> *J. Inst. Fuel*, 1945, **18**, 161, 193; B., 1945, I, 351.

<sup>72</sup> *Proc. Inst. Mech. Eng.*, 1944, **151**, 236; B., 1944, I, 55.

<sup>73</sup> *Nature*, 1945, **155**, 273; A., 1946, I, 281.

<sup>74</sup> *Z. Elektrochem.*, 1943, **49**, 178; B., 1945, I, 119.

<sup>75</sup> *J. Inst. Fuel*, 1945, **18**, 175; B., 1945, I, 351.



geometric structure. The accuracy of the method is increased considerably by this procedure. The mechanism by which a flame lights back clearly depends on the relationship between the flame speed and the issuing velocity of the air-gas mixture, but a further important factor is the "dead space" between the rim of the burner and the base of the inner cone. It is the gas velocity at the inside edge of the "dead space" which is all-important, and the greater is the "dead space" the smaller is the chance of light-back occurring. The most important points emerging from an investigation of "blow-off" were that the "blow-off" tendency of aerated burner flames decreases as the burner diameter increases, that double-cone flames are progressively more stable as the percentage of gas in the mixture is increased, and that of all three types of flame, those which are non-aerated are the most stable. Shadow photography has been used extensively in the investigation.

G. W. Jones and R. E. Kennedy,<sup>76</sup> in a report on the effects of pressure on the limits of inflammability of natural gas, have stated that the lower limit for gas-air mixtures is almost independent of pressure over the range 0—300 lb. per sq. in. The upper limit, however, is considerably affected, and rises with increase of pressure until at 350 lb. per sq. in. the inflammability range is 3.5 times that at atmospheric pressure.

M. A. Rivin<sup>77</sup> has described investigations on the influence of impurities on the development of detonation in the combustion of methane-air mixtures, which showed that the addition of only 0.3% by weight of ethylene was sufficient to cause detonation in a mixture in which it would not otherwise have occurred. Small amounts of light petroleum fractions generally had a similar effect, but benzene had not. It was also noted that in all cases where detonation was induced it had a spiral or spin motion. F. Schuster,<sup>78</sup> however, has stated that hydrocarbon-air mixtures of the type 50% methane-50% air, which are safe from explosion risks, could be produced with combustion characteristics and general properties, apart from density, similar to those of town's or grid gas, for which they are satisfactory substitutes.

A historical review of hydrocarbon flames, with a bibliography, has been published by J. R. Partington.<sup>79</sup>

At the same time as they were surveying the nature and quantities of organic sulphur compounds in town's gas, J. W. Wood and E. W. Claydon<sup>80</sup> examined the combustion characteristics of the gases. The object of the survey was to collect information regarding the chemical and physical properties of the gases as at present manufactured, and to ascertain the effect of variations in the coal carbonised and of the type

<sup>76</sup> U.S. Bur. Mines, 1945, Rept. Invest. 3798; B., 1945, I, 177.

<sup>77</sup> Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 500; A., 1945, I, 69.

<sup>78</sup> Gas- u. Wasserfach, 1944, 87, 25; B., 1945, I, 11.

<sup>79</sup> Ann. Sci., 1945, 5, 229.

<sup>80</sup> 47th Rept., Joint Res. Commee., Gas Res. Board and Univ. of Leeds; Gas Res. Board, 1945, Publ. G.R.B. 16.



of plant on those properties. The data obtained were intended, on the one hand, to assist the designers of appliances and, on the other, to furnish gas engineers with improved methods for the routine testing of their product. Gases from horizontal and vertical retorts were examined, together with blue and carburetted water-gas, and producer gas, and they were studied both in separate streams and in the various mixtures required for providing the declared calorific values of the several undertakings. When the calorific value of horizontal-retort gas is adjusted by dilution to equal that of the gas obtained by steaming the charges in vertical retorts, there is generally less difference between them than can be introduced by alternative diluents of the horizontal-retort gas. Carburetted water-gas has a considerably lower Aëration Test Burner (A.T.B.) number than have coal gases, and in mixtures exerts an influence rather greater than proportional to its concentration. Benzole washing has little influence on the A.T.B. number of the final gas, because it is compensated for by a smaller addition of diluent. The origin of the coal used affects the combustion characteristics far less than do the type of plant and the carbonising conditions. The report describes the use of the Aëration Test Burner to derive cone height-air-shutter opening ("CHASO") curves, with which an undertaking can readily control the quality of the gas distributed. Some tests with non-aërated burners, especially of the flare pressure, are described.

H. R. Hems<sup>81</sup> has reviewed the important part played by gas in the war industries. After describing the measures which were adopted to safeguard gas supplies to essential armament factories in an emergency, the author points out that in 1943 industrial sales over the country as a whole amounted to 35.1% of the total. Various applications of gas, in the manufacture of aircraft, tank, and vehicle components, guns, and shot, as well as machine tools, drop forgings, and castings, are detailed, and a concluding section describes the activities of the various Industrial Gas Centres.

The use of gas in processing glass tableware has been discussed by J. A. Tomes,<sup>82</sup> and A. G. Robiette<sup>83</sup> has developed a method for annealing whiteheart iron, in which incomplete combustion of gas results in a product of improved grain structure and increased hardness.

A. L. Roberts and R. Long<sup>84</sup> have investigated the mechanism of heating by radiation, with particular reference to the energy-wave-length distribution of commercially available radiators. The importance of this aspect is that gas-heated sources usually emit at longer wave-lengths than electrically-heated ones. Examination of the characteristics of

<sup>81</sup> *Inst. Gas Eng.*, 1945, *Comm.* 280.

<sup>82</sup> *Gas J.*, 1945, **245**, 123, 125, 147, 150, 153; *B.*, 1945, *I*, 100.

<sup>83</sup> *Inst. Brit. Foundrymen, Paper* 825; *B.*, 1945, *I*, 262. Cf. *B.P.* 571,245; *B.*, 1945, *I*, 398.

<sup>84</sup> 46th *Rept., Joint Res. Commee., Gas Res. Board and Univ. of Leeds; Gas Res. Board*, 1945, *Publ. G.R.B.* 15.



the principal refractory materials from which gas-heated radiators are made showed that their emission at short wave-lengths was considerably less than that for a black body at the same temperature. When, however, the comparison was made on the basis of equality of input, it was found that the radiator could emit at a rate approaching equality with the black body, but at temperatures which were necessarily far higher. Experiments on drying paint indicated that the wave-length distribution was of little significance except where the paint or underlying metal surface reflects appreciably. Most industrial materials are largely opaque to radiation, so that absorption occurs near the surface. When high surface temperatures are not desirable in articles undergoing treatment it is indicated that methods employing radiation may not offer advantages over the more conventional techniques.

The industrial use of gas-fired radiant heating has meanwhile continued to expand. It has enabled R. R. Gould, B. B. Evans, and A. M. Flannigan<sup>85</sup> to secure a reduction in the drying time in the manufacture of domestic china ware from 90—150 minutes to 12—15 minutes, with improved results; indirect economies obtained apart from the increase in throughput are also described. R. N. Green<sup>86</sup> has discussed other successful applications in the ceramic industry. Experiments with a multitubular infra-red oven on the drying of metal finishes have been published by W. A. Fitzsimmons,<sup>87</sup> and a comprehensive survey of the application of gas and electrical radiant heating to air circulation and conditioning, metal heating and finishing, tinplate production, evaporation processes, and the production of organic chemicals has been given by F. M. Tiller.<sup>88</sup>

Laboratory tests on the development of standards for evaluating the performance of water heaters have been described by L. Friedman.<sup>89</sup> U. Becher<sup>90</sup> has discussed improvements made in Germany in industrial and domestic gas appliances, whilst A. Forshaw<sup>91</sup> has reviewed the past forty years' work in the development of standards for the assessment of the performance of gas fires.

R. H. Anderson, D. C. Gunn, and A. L. Roberts<sup>92</sup> have described the construction and operation for various purposes of a number of gas-fired furnaces constructed with permeable walls through which the products of combustion were withdrawn. The advantages claimed for this design are that both the attainment and the maintenance of the working temperature require less fuel, that the temperature distribution is more uniform in the absence of streams leading to flue ports, and that, if

<sup>85</sup> *Bull. Amer. Ceram. Soc.*, 1945, **24**, 62; *B.*, 1945, **I**, 187.

<sup>86</sup> *Ibid.*, **8**; *B.*, 1945, **I**, 187.

<sup>87</sup> *Gas World*, 1945, **122**, *Ind. Gas Suppl.*, 39.

<sup>88</sup> *Chem. Products*, 1945, **8**, 35; *B.*, 1945, **I**, 202.

<sup>89</sup> *Gas J.*, 1945, **246**, 718, 721, 727, 731; *Gas World*, 1945, **123**, 446, 506.

<sup>90</sup> *Gas- u. Wasserfach*, 1943, **86**, 1; *B.*, 1945, **I**, 119.

<sup>91</sup> *Gas J.*, 1945, **245**, 601, 605, 631, 633.

<sup>92</sup> *J. Inst. Fuel*, 1944, **17**, 169; *Inst. Fuel War-Time Bull.*, 1945, *Oct.*, 19.



suitable refractories are available, very high temperatures are more easily attained. A theoretical discussion in support of the results is given.

K. Bunte and H. Brückner<sup>93</sup> have investigated, with a variety of gases, the relation between light emission from an incandescent mantle, the rate of gas supply, and the primary air:gas ratio. The maximum emission was found, not with the theoretical mixture, but with richer mixtures corresponding to the maximum primary combustion density. The gas:air ratio required to provide this emission was independent of the gas rate except at the lowest rates. These relationships were disturbed in the case of carbon monoxide by the addition of small concentrations of hydrogen or water vapour, an effect which was traced to the participation of hydrogen atoms and hydroxyl radicals in chain reactions in the combustion zone.

#### ANALYSIS AND TESTING.

J. Brown<sup>94</sup> has discussed the development of carbonisation assays, and has described his own (J.B./U.A.L.) test. He has attempted a correlation of the indications given by the several techniques which now exist and states that the results obtained are mainly determined by the method used for gas purification and the temperatures at which the assays are carried out. It is suggested that carbonisation assays could now with advantage be brought to the basis of an international standard, with at least three modifications to cover the range of commercial carbonising conditions. The author's opinion is that small-scale assays are of great value in the examination of the gas yield to be obtained from a coal, but for all other purposes at least semi-scale plant capable of carbonising 100 lb. of coal is essential; for examination of the coke, a full commercial charge is desirable. H. E. Blayden, J. Gibson, and H. L. Riley<sup>95</sup> have suggested the use of Caledon Jade Green or similar dibenzanthrone derivatives as carbonisation assay standards, as a result of comparative tests by the Fuel Research Board and J.B./U.A.L. methods.

In a symposium<sup>96</sup> held on methods for carbon and hydrogen determinations on coal, J. Brown and J. W. Binney described the Liebig method as more precise than that of Fenton for the hydrogen estimation, possibly on account of the different absorbent used for the water vapour, but less accurate for carbon. A. H. Edwards and M. Vahrman expressed the opinion that sulphur oxides are only removed completely in the Belcher method if the silver gauze is maintained at 700–800° throughout its length; if this is done, agreement with the British Standard method is satisfactory for carbon, hydrogen, and sulphur, but not for chlorine.

<sup>93</sup> *Gas- u. Wasserfach*, 1944, **87**, 31; *B.*, 1945, **I**, 11.

<sup>94</sup> *Inst. Fuel War-Time Bull.*, 1944, *Dec.*, 41; *Fuel*, 1945, **24**, 38; *C.*, 1945, 14.

<sup>95</sup> *Ibid.*, 1945, *Feb.*, 128; *C.*, 1945, 105.

<sup>96</sup> *Ibid.*, 1944, *Dec.*, 50, 57; *C.*, 1945, 89.



C. W. G. Ockelford<sup>97</sup> has given constructional details of an electric furnace designed for combustion at 800° in Fenton's method. W. Zimmerman<sup>98</sup> has suggested several modifications of the Pregl test, particularly the substitution of pumice impregnated with silver for silver wool, in order to secure greater efficiency and economy, and to minimise attack on the quartz combustion tubes. The changes proposed enable an unskilled operator to analyse 13 samples per 8-hour day.

S. D. Schmidt and W. Seymour<sup>99</sup> have detailed a rapid method of determining surface moisture in coal, in which the powdered sample is washed with ethyl or isopropyl alcohol, the liquid filtered off, and the water content calculated from the change in specific gravity; methyl alcohol is unsuitable since it also extracts some of the internal moisture. A. H. Edwards<sup>100</sup> has reviewed recent progress in the analysis and testing of solid fuels generally.

Improvements in the method of Grote and Krekeler for the determination of sulphur in liquid fuels (in which sulphur dioxide and trioxide are absorbed in 3% aqueous hydrogen peroxide and determined gravimetrically or volumetrically) have been suggested by H. Lehmann,<sup>101</sup> who recommends the use of an external evaporator connected by ground-glass joints to the combustion tube. Some of the air for combustion is passed through the evaporator; the bulk of the fuel is vaporised and the components of higher boiling point are distilled into the combustion tube. An accuracy of  $\pm 0.02\%$  was claimed.

P. Ashen<sup>102</sup> has described a rapid method for determining the potential tar in coke, in which a current of nitrogen passes over the dried graded sample heated in a silica tube and conveys the tar produced onto a filter-paper; the stain produced is compared with standards.

H. G. Pyke<sup>103</sup> has detailed the Australian Gas Light Company's method of evaluating the activity and fouling characteristics of iron oxides. Dry hydrogen sulphide is passed at a constant temperature through a layer of the finely-ground material containing 12.5% of moisture. The increase in weight is measured and the active iron value recorded is equivalent to the weight of hydrogen sulphide absorbed in 20 hours.

L. Ostermeier<sup>104</sup> has developed a new method for determining oxygen in town's gas; water is formed from it by reaction in the presence of a palladium-asbestos catalyst, and reacts subsequently with magnesium nitride, giving ammonia which is estimated. A. Demski<sup>105</sup> has found

<sup>97</sup> *Fuel*, 1945, 24, 64; C., 1945, 232.

<sup>98</sup> *Mikrochem.*, 1943, 31, 149; C., 1945, 210.

<sup>99</sup> *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3811; C., 1945, 165.

<sup>100</sup> *Brit. Coal Util. Res. Assoc. Bull.*, 1945, 9, 1; C., 1945, 233.

<sup>101</sup> *Oel u. Kohle*, 1943, 39, 880; C., 1945, 159.

<sup>102</sup> *Inst. Gas Eng.*, 1945, *Comm.* 281, 45; C., 1945, 165.

<sup>103</sup> *J. Proc. Austral. Chem. Inst.*, 1945, 12, 26; C., 1945, 95.

<sup>104</sup> *Gas- u. Wasserfach*, 1943, 86, 55; C., 1945, 93.

<sup>105</sup> *Ibid.*, 58; C., 1945, 93.



the new method more satisfactory than the pyrogallol method, and to give good agreement with the Lubberger-Broche method. K. Uhrig, F. H. Roberts, and H. Levin<sup>106</sup> have reported on a method whereby oxygen concentrations of between 0.001 and 5% can be measured, after the removal of sulphur dioxide, hydrogen sulphide, and mercaptans. The same authors<sup>107</sup> have described a method of determining traces (0.001%) of water vapour in hydrocarbon gases.

E. Berl, W. G. Berl, and G. A. Sterbutzal<sup>108</sup> have designed a "Thermo-barometer," which is an instrument for computing the weights of gases from their volumes, and which provides means for correcting observed to standard pressures and temperatures. F. Todd<sup>109</sup> has published details of an improved type of laboratory fractionating column capable of handling a wide volume range of sample (*i.e.*, from 2 c.c. to 5 litres) over the temperature range 0—400°, with an efficiency corresponding to a 30—50 theoretical plate column. V. C. Smith, A. L. Glasebrook, C. R. Begeman, and W. E. Lovell<sup>110</sup> have described an automatic laboratory-scale fractionating column, which has a 50 c.c. holdup on a 1200 c.c. per hour throughput, with an efficiency equivalent to that of a 120 theoretical plate column. A still-head which has been designed by L. Patrick<sup>111</sup> is regulated by mercury and is claimed to enable distillation rates as low as one drop in two minutes to be readily established.

<sup>106</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 31; C., 1945, 93.

<sup>107</sup> *Ibid.*, 212; C., 1945, 166.

<sup>108</sup> *Ibid.*, 166; C., 1945, 203.

<sup>109</sup> *Ibid.*, 175; C., 1945, 213.

<sup>110</sup> *Ibid.*, 47; C., 1945, 150.

<sup>111</sup> *Chem. and Ind.*, 1945, 74; C., 1945, 150.



## MINERAL OILS.

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AN important stage has been reached in the development of the chemical industry based on petroleum, particularly in the United Kingdom, owing to the removal of the high Customs duty on imported hydrocarbon oils used as raw materials for chemical synthesis. Indigenous oils used for this purpose will receive an allowance of Customs duty to the same amount so that they will have the same advantage over the imported oils as previously.<sup>1</sup> The removal of import duties on this raw material for the synthetic chemical industry should have an important effect on the growth of chemical industry together with other industries, such as synthetic plastics and fibres, which are dependent on supplies of synthetic chemicals in large quantities.

The petroleum industry, particularly the refining section, is a very large consumer of the products of the chemical industry.<sup>2</sup> Large quantities of sulphuric acid, caustic soda, and clays are used in refining gasoline and kerosine. For solvent extraction and dewaxing, sulphur dioxide, furfuraldehyde, phenol, acetone, etc. are used in very large quantities. A wide range of chemical products are used as catalysts and as additives for fuels and lubricants. It is important to stress that the requirements of chemicals for the petroleum industry are on a very large scale and extend over a wide field.

### NATURAL GAS.

The effect of pressure on the limits of inflammability of natural gas mixtures with air has been investigated and it has been found that for pressures below atmospheric the limits are practically the same as at atmospheric pressure.<sup>3</sup> For pressures above atmospheric, the lower limit of inflammability is practically independent of pressure for pressures up to 300 lb. per sq. in. The upper limit of inflammability, however, rises as the pressure is increased, so that an increase in pressure widens the range of inflammability, the range at 350 lb. pressure being 3.5 times that at atmospheric pressure.

The application of the Fischer-Tropsch synthesis to natural gas is receiving a great deal of attention, particularly in the United States.<sup>4</sup>

<sup>1</sup> *Petrol. Times*, 1945, 49, 291.

<sup>2</sup> R. Reuter, *Nat. Petrol. News*, 1945, 37, No. 1, 78R.

<sup>3</sup> G. W. Jones and R. E. Kennedy, *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3798; B., 1945, I, 177.

<sup>4</sup> A. L. Foster, *Oil and Gas J.*, 1945, 43, No. 36, 48.



In principle, the methane is oxidised, in the presence of a catalyst, to a mixture of carbon monoxide and hydrogen, and this mixture is heated in the presence of suitable catalysts, giving rise to the formation of hydrocarbons similar to those in petroleum. It is claimed that by this process good yields are obtained of gasoline of 75 octane number before the addition of lead tetraethyl. Under present conditions in the United States, natural gas is a more economical raw material than coal for the production of liquid hydrocarbons by the Fischer-Tropsch process, particularly when full use is made of the by-product gases for the manufacture of chemicals, but the process is not likely to compete with the present methods of producing gasoline from crude oil at present prices.<sup>5</sup>

### PETROLEUM SUBSTITUTES.

Information on the synthetic oil industry in Germany during the war period discloses the development of methods for increasing the aromatic content of synthetic gasoline made by the hydrogenation of coal.<sup>6</sup> The D.H.D. (Dehydrierung-hoch-Druck) process is carried out in a series of converters in which active alumina catalyst containing 10% of  $\text{MoO}_3$  is used and produces a gasoline fraction containing 65—68% of aromatics. This product blended with suitable light fractions gave a finished aviation gasoline having an octane value of 78 unleaded, or 87 with 0.09% by volume of lead tetraethyl.

An important development of the Fischer-Tropsch process is the "Iso-Synthesis" process whereby, in the presence of a catalyst at temperatures above  $200^\circ\text{C}$ . and pressures above 100 atmospheres, a  $\text{C}_3$ — $\text{C}_4$  fraction is obtained in which 90% of the  $\text{C}_4$  portion consists of isobutane.<sup>7</sup> This process was worked out at the Kaiser-Wilhelm Institute and has not yet been developed on a technical scale.

Another country which has embarked on the production of synthetic gasoline from brown coal is Spain, where construction has started near Zaragoza on a plant having a capacity of 100,000 tons of gasoline per annum.<sup>8</sup>

A method of producing liquid fuels from solid materials has been worked out experimentally in Russia, and is known as the "Thermal Solution" process.<sup>9</sup> The raw material, such as shale or peat, is ground to 0.2—5 mm., mixed with an equal weight of solvent, and heated at  $380$ — $430^\circ$  for 10—30 minutes at 30—40 atmospheres pressure. The mixture thus obtained is then distilled to separate various fractions for gasoline, Diesel fuel, etc. Solvents used are mazout, anthracene oil, tetralin, etc. It is claimed that a much higher proportion of organic matter is converted into liquid form than by other processes.

<sup>5</sup> G. G. Oberfell, *ibid.*, **44**, No. 32, 76.

<sup>6</sup> *Nat. Petrol. News*, 1945, **37**, No. 44, 4.

<sup>7</sup> F. Fischer, *Oel u. Kohle*, 1943, **39**, 517.

<sup>8</sup> *Petrol. Times*, 1946, **50**, 161.

<sup>9</sup> M. K. Djakova, *Compl. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 408, B., 1945, I, 54.



It is reported that it is proposed to increase the production of shale in the Lothians from 1,610,000 tons produced in 1944 to 2,500,000 tons per annum. New mines will be sunk and the refinery distilling capacity is to be extended to handle the increased production.<sup>10</sup>

The present production of gasoline from shale at Glen Davis in New South Wales is 2,500,000 gallons per annum at a cost of about 3s. 6d. per gallon. It is expected, after completion of extensions, that the production will amount to 9—10 million gallons per annum at a cost of about 1s. per gallon. It has been recommended that the commercial development of the Baerami shale deposits should not be carried on until further experience has been gained of the working at Glen Davis.<sup>11</sup>

In Belgium, motor-buses were successfully operated during the war on a fuel composed of coal gas and ammonia.<sup>12</sup> Compared with previous operation on gas oil there was no loss of power, no corrosion, and no increase in lubricating oil consumption it is claimed, but the compression ratio used was 8.5 : 1 compared with 16 : 1 used originally with gas oil.

#### REFINERY PLANT.

The longest pipe-line in the world is now in operation pumping gasoline and Diesel fuel from Calcutta to Kunming in China, a distance of 1800 miles.<sup>13</sup> This line is 400 miles longer than the famous "big inch" pipe-line connecting Longview in Texas with Philadelphia and New York.

As a war measure a series of pipelines were constructed across the English Channel, so that gasoline could be pumped from the British coast to points in Northern France for supply to the troops.<sup>14</sup> The scheme, known as "Pluto," enabled as much as one million gallons daily to be pumped across the Channel, a total of 172 million gallons being transported in this way before the closing down of these operations.

The storage and transport of large quantities of liquids, such as mineral oils, involves the use of methods of measurement which should be standardised. The Institute of Petroleum have published details of methods of measurement of oil in tanks and pipelines which will eventually be issued, revised if necessary, as standard methods.<sup>15</sup>

The separation of hydrocarbons by fractional distillation is an important operation in the manufacture of petroleum products. In recent years the process known as "extractive" distillation has been used for the separation of nitration-grade toluene from mixtures with other hydrocarbons.<sup>16</sup> This process involves the addition of a solvent which has a higher boiling point and is selective for one component. The more

<sup>10</sup> *Chem. Eng. News*, 1945, 23, 1784.

<sup>11</sup> *Chem. Age*, 1945, 53, 56.

<sup>12</sup> E. Kroch, *J. Inst. Petroleum*, 1945, 31, 213; B., 1945, I, 320.

<sup>13</sup> *Petrol. Times*, 1945, 49, 533.

<sup>14</sup> V. A. Sheals, *Oil and Gas J.*, 1954, 44, No. 20, 205; *Petrol. Times*, 1945, 49, 433.

<sup>15</sup> *J. Inst. Petroleum*, 1945, 30, 40.

<sup>16</sup> *Ann. Repts.*, 1943, 28, 70.



volatile component distils over, leaving a residue of the second component with the solvent which can be fractionated in a second stage and the solvent may be used again for the operation.<sup>17</sup> A suitable solvent for the separation of toluene from associated hydrocarbons in phenol.<sup>18</sup> An important advantage of extractive distillation over azeotropic distillation is that the heat input for a given separation is lower because solvent is not distilled off.<sup>19</sup>

### CRACKING.

A study of the behaviour of pure hydrocarbons under catalytic cracking conditions shows that the results obtained differ considerably from the results of thermal cracking. In general, it was found that catalytic cracking of paraffin hydrocarbons at 500° c. gave much faster rates of cracking than did thermal operations, particularly for hydrocarbons of high molecular weight. The catalytic process yielded products containing more aromatic and branched-chain aliphatic hydrocarbons.<sup>20</sup> In the case of naphthenes the hydrocarbons produced were more saturated than those from paraffin hydrocarbons, and there was a tendency for isomerisation of the six-ring to the five-ring hydrocarbons. There was also a considerable production of aromatic hydrocarbons.<sup>21</sup> When aromatic hydrocarbons were cracked in the presence of a catalyst the fission took place at the bond next to the aromatic ring instead of in the side-chain itself. In general, the investigation into the cracking of hydrocarbons by the two methods leads to the conclusion that the presence of a catalyst produces less of the C<sub>1</sub> and C<sub>2</sub> hydrocarbons, less unsaturation, less diolefines, and a greater production of aromatics and coke.<sup>22</sup>

In order to make catalytic cracking a practical operation for small refineries, a plant of small capacity has been designed. The cost of construction and operation of this plant—known as the M.S. type—has been considerably reduced by the incorporation of the reactor and regenerator into the same tower. The catalyst used is a micro-spherical synthetic product based on silica-magnesia or silica-alumina.<sup>23</sup> Catalytic cracking units of capacity as small as 500 barrels per day have been designed.<sup>24</sup>

The formation of carbon on the catalyst during catalytic cracking has been studied for both fixed bed and fluid catalyst conditions, using natural and synthetic catalysts. Although the rate of carbon deposition depends on a number of factors, it has been shown that the rate of carbon

<sup>17</sup> B.P. 563,122; B., 1944, I, 351.

<sup>18</sup> C. L. Dunn, R. W. Millar, G. J. Pierotti, R. M. Shiras, and M. Souders, jun., *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 631; B., 1946, I, 88.

<sup>19</sup> I. Benedict and L. C. Rubin, *ibid.*, 353; B., 1945, I, 346.

<sup>20</sup> B. S. Greensfelder and H. H. Voge, *Ind. Eng. Chem.*, 1945, **37**, 514.

<sup>21</sup> *Ibid.*, 1039; B., 1946, I, 70.

<sup>22</sup> *Ibid.*, 1168; B., 1946, I, 151.

<sup>23</sup> L. K. Anderson and M. J. Sterba, *Oil and Gas J.*, 1945, **44**, No. 33, 77.

<sup>24</sup> G. Egloff, *Nat. Petrol. News*, 1945, **37**, No. 41, 50.



deposition is relatively independent of the feed rate and is approximately a logarithmic function of the length of time since the catalyst was last regenerated.<sup>25</sup>

### MOTOR SPIRIT.

Details of the production of aviation gasoline in Britain during the war period have been published.<sup>26</sup> The commercial production of isooctane was started in 1939, using as a feedstock a  $C_4$  polymer fraction which was subjected to hydrogenation. Base-stock for blending high-quality aviation gasoline was produced by the hydrogenation of creosote at the Billingham plant, but the main contribution of base-stock was from a plant where imported gas oil was subjected to "splitting" hydrogenation. A by-product from the latter process was isobutane, which was dehydrogenated to isobutene, then polymerised to diisobutene, and hydrogenated to isooctane. A valuable component for aviation gasoline, giving high rich mixture performance, is butylbenzene ("Vic-tane"), made by the alkylation reaction of butene and benzene. This component is manufactured in Britain and is used for the production of aviation gasoline having an octane number in excess of 100.

The use of water and mixtures of methanol and water for improving combustion conditions has received considerable attention.<sup>27</sup> For the most economical results, a blend of equal parts of methanol and water is recommended. This mixture acts as an "internal coolant," the latent heat of evaporation lowering the temperature of the charge and suppressing detonation. By this means it is possible to get higher power output for conditions obtaining at take-off for aircraft.

The use of gasolines of high octane value for aviation fuel has made it necessary to introduce methods of measuring the octane number of fuels above 100. The Institute of Petroleum has proposed the use of isooctane + 4 ml. of lead tetraethyl per Imperial gallon as a primary reference fuel corresponding to an octane number of 120.<sup>28</sup> It is recommended that the "17° Motor Method"<sup>29</sup> should be modified by using a fixed spark setting of 25° advance as this would enable a continuous scale to be obtained for the range of octane numbers from 40 to 120.<sup>30</sup> Proposals have also been made to use triptane ( $\beta\beta\gamma$ -trimethylbutane), and heptane to which lead tetraethyl has been added, as primary fuels for establishing a scale by which aviation fuels of high octane number can be measured.<sup>31</sup>

The use of turbine-jet aircraft is not economical in fuel consumption for speeds below about 500 miles per hour except at high altitudes above

<sup>25</sup> A. Voorhies, *Ind. Eng. Chem.*, 1945, 37, 318; B., 1945, I, 250.

<sup>26</sup> *Petrol. Times*, 1945, 49, 423.

<sup>27</sup> A. T. Colwell, R. E. Cummings, and D. E. Anderson, *Nat. Petrol. News*, 1945, 37, No. 6, 88R.

<sup>28</sup> *J. Inst. Petroleum*, 1945, 31, 48.

<sup>29</sup> *Ann. Repts.*, 1941, 26, 76.

<sup>30</sup> L. B. Sweetland and P. Draper, *J. Inst. Petroleum*, 1945, 31, 105.

<sup>31</sup> D. B. Brooks, *Refiner*, 1946, 25, No. 1, 130.



40,000 feet.<sup>32</sup> For speeds between 200 and 600 miles per hour at normal altitudes, the most efficient power unit for aircraft is a combination of gas turbine and propeller.<sup>33</sup>

### LUBRICATING OILS.

In order to get some insight into the cause of piston-ring sticking in a spark-ignition engine the deposits on the rings were analysed and found to consist mainly of oxyacids and their derivatives and insoluble material derived from the condensation of oxyacids.<sup>34</sup> Anti-ring-sticking agents, such as aluminium dinaphthenate, aluminium stearate, and calcium dichlorostearate, are effective as they react with oxyacids to form inert soaps which are dissolved or dispersed in the lubricating oil.

The corrosive effect of lubricating oils in service can be considered under two conditions: "existent corrosivity," which is due to the chemical composition of the lubricant, and "potential corrosivity," which occurs under conditions representing actual service and is the result of the oxidation of the oil.<sup>35</sup> The existent corrosivity is measured by the loss in weight, as mg. per sq. cm., of a sample of the metal chosen when subjected to immersion in the lubricating oil at a temperature of 313° F. for 20 minutes. For measuring the potential corrosivity, a thrust-bearing corrosion machine is used<sup>36</sup> consisting of a steel cup in which a steel disc is made to rotate against three flat bearing specimens of the metal chosen for the test. The potential corrosivity is measured by the loss in weight of the bearing metal specimens after operating the steel disc at 2400 r.p.m. for 20 hours at 225° F. using 35 c.c. of the lubricating oil under examination.

A simple method of testing the used lubricating oil has been introduced, which can be applied to determine when a change of lubricating oil is desirable during actual operation.<sup>37</sup> A lead-plated copper strip is used, the lead being deposited in seven half-inch "steps" varying in thickness from 3 to  $100 \times 10^{-6}$  inch. The strip can be attached to a dip-stick and the measurement can be made without removing the oil from the crankcase of the engine. A convenient time for the immersion of the strip in the crankcase is one hour when the temperature of the oil is at 280° F. The amount of corrosion is measured by the number of "steps" of lead which are removed during the test. It is suggested that the removal of two steps in one hour, under the test conditions, represents incipient corrosion, and four or more steps correspond to definite corrosion.

<sup>32</sup> Lord Winster, *The Times*, 1945, Oct. 19.

<sup>33</sup> C. D. Flagle and F. W. Godsey, jun., *Petroleum*, 1945, 8, 174.

<sup>34</sup> G. H. Denison, jun., and J. O. Clayton, *J. Soc. Auto. Eng.*, 1945, 53, 264r.

<sup>35</sup> G. W. Waters and H. D. Burnham, *Ind. Eng. Chem.*, 1944, 36, 263; B., 1944, I, 220; C., 1944, 116.

<sup>36</sup> S. E. Talley, R. G. Larsen, and W. A. Webb, *Ind. Eng. Chem. [Anal.]*, 1945, 17, 168; C., 1945, 219.

<sup>37</sup> R. G. Larsen, F. A. Armfield, and L. D. Grenot, *ibid.*, 19; C., 1945, 100.



A source of trouble in the operation of aero-engines is the formation of a stable foam in the lubricating oil, particularly when operating at high altitudes. The presence of foam may cause stoppage in the flow of oil through the supply channels and may also cause considerable loss of oil by leakage through the breather outlets. The higher alcohols, such as octyl alcohol, have been used as additives to prevent heavy foaming during chemical reactions in industrial processes.<sup>38</sup> Anti-foaming additives have been used successfully in lubricating oils,<sup>39</sup> but very little information has been disclosed on the actual materials used for this purpose. The use of silicones as antifoaming agents has been claimed,<sup>40</sup> and other substances proposed are potassium oleate in sulphurised sperm oil,<sup>41</sup> and barium diethylhexyl or barium ditetradecyl dithiophosphates.<sup>42</sup>

Polymers of organo-silicon oxide (silicones)<sup>43</sup> have been prepared which have a wide range of application. They have good dielectric, water-repellent, and heat-stable characteristics; they also have high viscosity index and they can be used for high-temperature lubricants and for insulating and chemical-resisting greases.

### FUEL OIL.

The use of a high-speed camera, taking 5000 pictures per second, has been applied in the past to the study of combustion in spark-ignition engines.<sup>44</sup> This type of camera has recently been used to investigate the combustion process in Diesel engines.<sup>45</sup> The cinematograph films obtained with the high-speed camera, at the rate of 40,000 pictures per second, are recorded and screened at the rate of 16—24 pictures per second, that is, at a rate 2500 times slower than the actual duration of the combustion reaction. By this means it has been demonstrated that the multiple-orifice nozzle gives better fuel distribution than the single-orifice nozzle and that Diesel knock develops with increasing injection advance angle.

The use of amyl nitrate as an additive for improving the cetane number of Diesel fuels does not have an appreciable effect on the Diesel index, which is given by the formula:  $\text{aniline point } ^\circ\text{F.} \times \text{gravity}^\circ\text{A.P.I.}/100$ . The Diesel index has, therefore, no relationship with cetane value in cases where an addition agent such as amyl nitrate is used.<sup>46</sup>

A large proportion of the fuel oil for domestic burners in the United States is being supplied by distillate from the catalytic cracking process.

<sup>38</sup> *Ann. Repts.*, 1938, 23, 122.

<sup>39</sup> H. A. Ambrose and C. E. Trautman, *J. Soc. Auto. Eng.*, 1945, 53, 373.

<sup>40</sup> T. A. Kauppi and W. W. Pederson, *Nat. Pet. News*, 1945, 37, No. 49, 945R.

<sup>41</sup> U.S.P. 2,377,654.

<sup>42</sup> U.S.P. 2,368,000.

<sup>43</sup> U.S.P. 2,258,218—22.

<sup>44</sup> *Ann. Repts.*, 1936, 21, 87.

<sup>45</sup> C. D. Miller, *J. Soc. Auto. Eng.*, 1945, 53, 719.

<sup>46</sup> *World Petrol.*, 1946, 17, No. 1, 42.



This type of fuel oil, owing to the presence of a relatively high proportion of aromatics, has a tendency to smoke and is sensitive to draughts compared with straight-run distillate fuel when used in pot type burners. It has been demonstrated that fuels from catalytic cracking plants require a longer time for mixing with air before the oil is exposed to the high temperature of the combustion chamber. Suitable burners for this type of fuel oil have been designed.<sup>47</sup>

#### ASPHALTIC BITUMEN.

The extracts obtained by treating lubricating oil stocks with solvents such as phenol, nitrobenzene, propane-cresol mixtures, or furfuraldehyde are viscous, aromatic materials which react with sulphur. The sulphurised substances obtained by heating 60% of extract and 40% of sulphur at 170—180° c. for 6—8 hours are asphaltic in type and have properties similar to blown asphaltic bitumen. Suitable catalysts, which shorten the time for this reaction, are red phosphorus and phosphorus pentachloride.<sup>48</sup> The asphaltic materials obtained by this process have a flat penetration-temperature curve and are claimed to be suitable for use as joint fillers or caulking compounds.

A blown type of asphaltic bitumen can also be obtained by blending asphaltic bitumen with powdered rubber or with rubber latex.<sup>49</sup> Such asphaltic materials can be used as partial replacement of natural or synthetic rubber.

The asphaltene, resin, and oily constituent fractions of asphaltic bitumen have been examined with regard to their dielectric constants and behaviour on dissolution.<sup>50</sup> It is concluded that the asphaltenes and resins are polar and the oily constituents non-polar. Further work is being carried out on this subject in order to obtain information on the molecular composition of asphaltic bitumen.

#### SPECIAL PRODUCTS.

The petroleum chemical industry is based very largely on the supply of olefinic gases from the cracking process. Gas from thermal cracking may contain from 12 to 25% of C<sub>3</sub> and lighter olefines. A typical cracked gas from this source would yield 5.8% of ethylene and 10.5% of propylene. Gas from the fluid catalytic cracking process may contain 9% of C<sub>3</sub> and lighter olefines, of which the propylene may be 30—50%. This gas fraction may vary from 6 to 14.5% by weight.<sup>51</sup>

It is reported that a new plant in Texas for the production of nylon will be supplied with its intermediate chemicals, adipic acid and hexamethylenediamine, made from cyclohexane obtained as a fraction from

<sup>47</sup> *World Petrol.*, 1946, **17**, No. 1, 56.

<sup>48</sup> P. V. McKinney, M. G. Mayberry, and H. E. Westlake, *Ind. Eng. Chem.*, 1945, **37**, 122; B., 1945, I, 177.

<sup>49</sup> D. C. Broome, *J.S.C.I.*, 1945, **64**, 149; B., 1945, I, 210.

<sup>50</sup> J. M. Swanson, *J. Physical Chem.*, 1942, **46**, 141.

<sup>51</sup> *Chem. Met. Eng.*, 1945, **52**, No. 12, 121.



petroleum naphtha where it is present to the extent of 1—4%. The hydrogen required for the process will be manufactured from natural gas.<sup>52</sup>

Another new chemical plant in Texas in which natural gas is the basic raw material has recently started operations.<sup>53</sup> The principal products made are acetic acid, acetic anhydride, acetone, methanol, and formaldehyde. Another portion of the plant is used for the manufacture of butadiene for synthetic rubber.

A process has been developed to the pilot-plant stage for the manufacture of organic nitrogen compounds by the direct interaction of olefines and ammonia in the presence of a suitable catalyst.<sup>54</sup> Starting with ethylene and propylene, acetonitrile, propionitrile, and butyronitrile are obtained as primary products. Acrylonitrile, which can be made by this process, is used for co-polymerisation with butadiene for the production of oil-resistant synthetic rubbers.

Toluene has been produced from petroleum by the dehydrogenation of a suitable fraction of a naphthenic straight-run gasoline, consisting mainly of methylcyclohexane.<sup>55</sup> By the use of a molybdena-alumina catalyst in the presence of hydrogen, it is possible to isomerise and dehydrogenate dimethylcyclopentane directly to toluene, so that a wider gasoline fraction can be used comprising dimethylcyclopentanes as well as methylcyclohexane.<sup>56</sup>

A combination of cyclisation and dehydrogenation, that is, the aromatisation of open-chain paraffins, can be accomplished by heating in the presence of  $\gamma$ -alumina incorporating chromium oxide ( $\text{Cr}_2\text{O}_3$ ). This method can be used to convert *n*-heptane into toluene.<sup>57</sup>

Phthalic anhydride is an important intermediate product for the manufacture of anthracene derivatives such as anthraquinone dyes. In the past phthalic anhydride has been manufactured from naphthalene obtained from coal tar, but recently a factory has started operating in California for the production of phthalic anhydride from *o*-xylene which is obtained when petroleum fractions are subjected to the catalytic hydroforming process for the production of toluene as the main product. It is probable that petroleum-toluene plants, using the hydroforming process, can be adjusted for the primary production of *o*-xylene, so that this would provide a useful outlet for the surplus toluene plants built during the war, while at the same time leaving the possibility of re-conversion to toluene production if this should be required in an emergency.<sup>58</sup>

<sup>52</sup> *Nat. Petrol. News*, 1945, 37, No. 36, 742R.

<sup>53</sup> *Chem. Trade J.*, 1945, 117, 363.

<sup>54</sup> *Oil and Gas J.*, 1945, 44, No. 16, 150.

<sup>55</sup> *Ann. Repts.*, 1943, 28, 70.

<sup>56</sup> B.P. 571,543; B., 1945, I, 381.

<sup>57</sup> B.P. 564,187; B., 1944, II, 345.

<sup>58</sup> *Chem. Trade J.*, 1945, 116, 250.



The production of carbon black is expanding at a great rate owing to the heavy demand for rubber tyres. 90% of the consumption of carbon black in the United States is used in the rubber industry as it is considered to be the best reinforcing pigment known for rubber tyres. The production of carbon black in the United States in 1938 amounted to 477 million lb., in 1944 it was 991 million lb., and it was expected that the production for 1945 would be 1240 million lb.<sup>59</sup>

#### ANALYSIS AND TESTING.

The sixth edition of "Standard Methods for Testing Petroleum and its Products" was published by the Institute of Petroleum in 1945. This edition contains a number of additional tests for asphaltic bitumen and also new methods for the estimation of hydrogen sulphide in gases and distillates, for mercaptan-sulphur in light distillates, and total sulphur in gases and distillates. There is an appendix dealing with the principles of oil measurement based on recommendations made by the Institute of Petroleum in collaboration with the American Society for Testing Materials.

The method of estimating aromatic hydrocarbons in gasoline by filtration through silica gel<sup>60</sup> has been extended to the separation and estimation of aromatic and mono-olefine hydrocarbons in mixtures with paraffins and naphthenes.<sup>61</sup> When the mixture to be analysed is introduced into a column of silica gel and a suitable desorbing liquid is added, the components leave the bottom of the column in the following order: paraffin plus naphthene, mono-olefine, and aromatic hydrocarbons. The composition of the original mixture can be determined by measuring the amount of each fraction.

A method of measuring the viscosity of oils at temperatures down to  $-50^{\circ}\text{C}$ . is based on the Ubbelohde-Holde viscometer. The oil under test is introduced into the U-tube and dyed methyl or ethyl alcohol is poured on to the top of the oil. The times are noted for the alcohol to fill the bulb between marks under the application of pressure and for the alcohol to be emptied from the bulb when the pressure is reversed. The absolute viscosity  $\eta$  is calculated from the usual expression  $\eta = cPt$ , where  $P$  is the pressure in mm. of mercury,  $t$  is the mean time of flow in seconds, and  $c$  is the constant for the viscometer. It is claimed that the accuracy of the method is within 0.5%. The method may also be applied to the determination of the absolute viscosity of opaque petroleum products at higher temperatures using a higher alcohol.<sup>62</sup>

The estimation of water in hydrocarbon gases can be carried out by absorbing the water in carefully dried acetone at  $-57^{\circ}$  to  $-62^{\circ}\text{C}$ . and adding excess of acetyl chloride in toluene. The unused acetyl chloride

<sup>59</sup> *Oil and Gas J.*, 1945, 44, No. 8, 132.

<sup>60</sup> *Ann. Repts.*, 1944, 29, 72.

<sup>61</sup> B. J. Mair, *J. Res. Nat. Bur. Stand.*, 1945, 34, 435; *C.*, 1945, 236.

<sup>62</sup> Y. A. Pinkevich, *Petroleum*, 1945, 8, 214.



is decomposed by ethyl alcohol and the liberated acids are titrated with standard caustic soda solution.<sup>63</sup>

A reagent which is claimed to be superior to a solution of silver sulphate in sulphuric acid for the estimation of ethylene is a solution containing 22% of mercuric sulphate in 22% sulphuric acid, having a specific gravity of 1.37. This reagent absorbs ethylene irreversibly, does not attack paraffins, and does not absorb carbon monoxide or hydrogen. As the reagent absorbs other olefines and carbon dioxide, these must be removed by the use of sulphuric acid and caustic potash, prior to the ethylene absorption.<sup>64</sup>

The various methods of estimating lead tetraethyl in gasoline have been reviewed<sup>65</sup> and the two methods recommended involve the direct evaporation of the sample with a decomposition agent. The lead tetraethyl is converted into inorganic lead by mixing with hydrochloric acid or iodine, evaporating the resulting mixture to dryness, and removing the organic matter by oxidation with nitric, perchloric, or sulphuric acid. The lead in the inorganic residue is determined with dichromate solution. The reproducibility of the methods is within 0.01 ml. of lead tetraethyl per American gallon of gasoline or 0.4% of lead in ethyl fluid.

A comparison has been made between the results obtained for the "existent" gum content in gasoline when determined by the methods of the Institute of Petroleum (I.P.-38/44(T)) and the American Society for Testing Materials (A.S.T.M.-D.381-44). Both the evaporation temperature and air flow rates are higher for the A.S.T.M. method than for the I.P. method, and there are other differences in details.<sup>66</sup> It was found that the ratio between the values by the I.P. method and the A.S.T.M. method was 1.33. This ratio appears to be constant for all gasolines within the error of the test, and it is independent of the gum content, the composition of the gasoline, the boiling range, or the presence of additives such as lead tetraethyl.

The "lamp" method for the estimation of sulphur in petroleum distillates has been investigated and a new lamp developed which gives rapid and smokeless combustion even when the sample has a high aromatic content.<sup>67</sup> The method evolved has been adopted by the Institute of Petroleum as a tentative standard method for sulphur determination.<sup>68</sup> By using a turbidimetric method for titrating the absorber solution it is possible to estimate the sulphur content when it is as low as 0.0001% by weight.

<sup>63</sup> H. Levin, K. Uhrig, and F. M. Roberts, *Ind. Eng. Chem. [Anal.]*, 1945, 17, 212; C., 1945, 166.

<sup>64</sup> A. W. Francis and S. J. Lukasiewicz, *ibid.*, 703; C., 1946, 16.

<sup>65</sup> L. Lykken, R. S. Treseder, F. D. Tuemmler, and V. Zahn, *ibid.*, 353; C., 1945, 233.

<sup>66</sup> E. L. Walters and D. L. Yabroff, *Amer. Soc. Test. Mat.*, 1945, *Bull.* 135, 40.

<sup>67</sup> A. R. Javes, *J. Inst. Petroleum*, 1945, 31, 129; C., 1945, 159.

<sup>68</sup> I.P. Method 107/45 (Tentative).



# INTERMEDIATES AND COLOURING MATTERS.

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THE year under review is very similar to those that immediately preceded it, the volume of publication being still seriously below normal owing to war "blackout." The major number of published patents are American, and in most cases are the results of work carried out before the entry of the U.S.A. into the war. British and, in general, European scientific progress is very much obscured by restrictions on publications, and a full discussion will not be possible again until restrictions are lifted. It does, however, seem to be clear that no major effort on colouring matters has been necessary in the past six years in any way comparable with that which took place during and after the war of 1914-18. We may therefore in the immediate future expect increased publications in branches of organic chemistry other than dyestuffs.

## INTERMEDIATES.

### *Halogen Derivatives.*

H. C. Brown<sup>1</sup> contributes a useful summary of the properties of sulphuryl chloride for the halogenation of different classes of organic compounds, either alone for reactive compounds or with the aid of benzoyl peroxide for saturated aliphatic hydrocarbons. The introduction of the  $\cdot\text{SO}_2\text{Cl}$  group by means of aluminium chloride for aromatic and by light and pyridine for aliphatic compounds is also reviewed. In certain cases also sulphuryl chloride acts as an acylating agent, for example, with alcohols and metal derivatives of acetaryl amides.

Nitromethane dissolved in carbon tetrachloride or preferably trichloronitromethane reacts smoothly, according to Commercial Solvents Corporation,<sup>2</sup> with chlorine and aqueous caustic soda added simultaneously, while avoiding any excess of alkali; the product consists of 36% of chloronitromethane and the rest is trichloronitromethane.

Chlorination of olefines occurs to some extent, according to A. D. Little, Inc.,<sup>3</sup> when they are treated with a *tert.*-alkyl hypohalite. Thus, isobutene in acetic acid solution at 0° with *tert.*-butyl hypochlorite yields  $\text{CMe}_2\text{CHCl}$  and  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OAc}$ .

Imperial Chemical Industries<sup>4</sup> describe the preparation of trichloroacetonitrile by the chlorination of acetonitrile in the vapour phase with a non-volatile catalyst of activated carbon, impregnated with zinc,

<sup>1</sup> *Ind. Eng. Chem.*, 1944, **36**, 785; B., 1945, II, 1.

<sup>2</sup> U.S.P. 2,181,411; B., 1944, II, 341.

<sup>3</sup> U.S.P. 2,179,787; B., 1944, II, 342.

<sup>4</sup> B.P. 567,289; B., 1945, II, 168.



copper, or barium chloride. The product forms a trimer, b.p.  $155^{\circ}$ , m.p.  $59^{\circ}$ , and a tetramer, b.p.  $170^{\circ}$ , m.p.  $77^{\circ}$ . By scrubbing in a tower with water, partial dechlorination occurs and the lower acetonitriles are formed, yielding a mixture which may be separated by fractionation.<sup>5</sup>

### *Ethylene Oxide.*

E. T. McBee, H. B. Haas, and P. A. Wiseman<sup>6</sup> discuss a study of the oxidation of ethylene over a silver-corundum catalyst, including the effect of operational variables. For 1 second contact, the optimum temperature with the new catalyst is  $268^{\circ}$ , giving 40—50% conversion; after 4 weeks the optimum is  $280^{\circ}$  with a 30—40% conversion. Conversion and yield increase with increasing air to ethylene ratio, 10:1 being normally used. A small addition of dichloroethane greatly improves the yield, but larger amounts poison the catalyst.

Distillers Co. Ltd.<sup>7</sup> absorb ethylene oxide from the dilute gas mixture in water, and then treat the latter with air or inert gas under partial vacuum, giving a gas with a higher ethylene oxide content than the original; this is then absorbed at normal pressure in a smaller volume of water, the process being carried out countercurrentwise in towers.

U.S. Industrial Alcohol Co. absorb the ethylene oxide in water, remove it with steam, and convert the effluent gas into glycol in presence of a catalyst<sup>8</sup> or pass it over an active carbon absorbent.<sup>9</sup>

### *Carboxylic Acids.*

Imperial Chemical Industries and E. I. Du Pont de Nemours & Co.,<sup>10</sup> in related cases, describe the hydrolysis of alkyl glycolates to yield an aqueous acid product which is worked up by evaporating to dryness by an extremely rapid method, giving an acid with less than 6% of polymer.

The manufacture of adipic acid (mainly for nylon manufacture) is responsible for a number of patents. The oxidation of *cyclohexanol* is the chief method employed. The raw material may be prepared according to Imperial Chemical Industries<sup>11</sup> by reduction of benzene with hydrogen over a catalyst under pressure at temperatures from  $180^{\circ}$  to  $250^{\circ}$  to *cyclohexane*; the latter is then oxidised catalytically, yielding both *cyclohexanol* and *cyclohexanone*. The conversion of the latter into adipic acid by oxygen using a manganese and barium acetate catalyst in the liquid phase in presence of a solvent (acetic acid) is described by E. I. Du Pont de Nemours & Co.<sup>12</sup> *cycloHexanol* may be oxidised in the liquid phase under pressure by oxygen in a similar way, the catalyst being acetates of cobalt, copper, or manganese, but an initiator is also required, for

<sup>5</sup> B.P. 568,670; B., 1945, II, 236.

<sup>6</sup> *Ind. Eng. Chem.*, 1945, 37, 432; B., 1945, II, 289.

<sup>7</sup> B.P. 564,646; B., 1945, II, 4. Cf. B.P. 533,054; B., 1941, II, 175.

<sup>8</sup> U.S.P. 2,325,576; B., 1945, II, 289.

<sup>9</sup> U.S.P. 2,325,577; B., 1945, II, 289.

<sup>10</sup> B.P. 567,237, 567,575; B., 1945, II, 164.

<sup>11</sup> B.P. 570,042; B., 1945, II, 295.

<sup>12</sup> B.P. 566,110; U.S.P. 2,316,543; B., 1945, II, 71, 52.



instance a peroxide.<sup>13</sup> On the other hand, *cyclohexanol* is oxidised readily with nitric acid, and Imperial Chemical Industries<sup>14</sup> and A. M. Moronow and C. A. Miketta<sup>15</sup> describe similar continuous processes where *cyclohexanol* and nitric acid are continually added to a reaction mixture while a corresponding amount of the mixture is continuously withdrawn, cooled, and filtered from the adipic acid and recycled into the process if desired. Imperial Chemical Industries specify a vanadium catalyst for this process. *cycloHexene* may be obtained from petroleum fractions, and the Tide Water Associated Oil Co.<sup>16</sup> describe its oxidation with nitric acid in presence of a vanadium, molybdenum, or chromium compound to yield adipic acid. It is not surprising to note that the Shell Development Co.<sup>17</sup> describe a continuous process for oxidation of *cyclopentanol* to glutaric acid by nitric acid.

The manufacture of oxalic acid by nitric acid oxidation of carbohydrates, although an old and well-known process, has been reinvestigated and standardised by General Chemical Co.<sup>18</sup> Typically, starch is first hydrolysed by boiling with 11% oxalic acid, and then oxidised, in presence of mother-liquor of a previous batch, with sulphuric-nitric acid and a vanadium catalyst; on cooling, a yield of 1.653 parts of oxalic acid is obtained from 1 part of starch.

By-product chlorinated hydrocarbon mixtures offer a cheap source of maleic or fumaric acid, when oxidised continuously in the vapour phase over a vanadium catalyst, as described by W. L. Faith,<sup>19</sup> and in addition hydrochloric acid is recoverable.

Celanese Corporation of America<sup>20</sup> describe a continuous vapour-phase process for oxidising a mixture of an aldehyde and air or oxygen to the corresponding per-acid. Only partial conversion is permitted, and the product is extracted with benzene and azeotropically distilled. Peracetic acid is so prepared in a 30% conversion from acetaldehyde.

## COLOURING MATTERS.

### Azo-DYES.

The majority of specifications which are considered in this review, covering the period November, 1944, to October, 1945, inclusive, are of American origin, and all of these relate to azo investigations which were carried out before America entered the war. The main fields of activity to which the patents reviewed relate are those concerned with direct cotton dyes and dyes for acetate rayon. In the latter category provision is often now made for the use of such dyes for the colouring of nylon.

<sup>13</sup> B.P. 565,636; B., 1945, II, 46.

<sup>14</sup> B.P. 567,325; B., 1945, II, 166.

<sup>15</sup> U.S.P. 2,191,786; B., 1945, II, 236.

<sup>16</sup> U.S.P. 2,323,861; B., 1945, II, 260.

<sup>17</sup> U.S.P. 2,193,562; B., 1945, II, 260.

<sup>18</sup> U.S.P. 2,322,915; B., 1945, II, 204.

<sup>19</sup> *Ind. Eng. Chem.*, 1945, 37, 438; B., 1945, II, 289.

<sup>20</sup> U.S.P. 2,314,385; B., 1944, II, 343.



There have been practically no new developments in azo-dyes for wool and leather and few in the azoic field apart from various new methods of stabilisation of diazo-compounds.

### General.

R. N. Shreve, R. P. Carter, and J. M. Willis<sup>21</sup> have described the diazotisation of aminoguanidine and given optimum conditions for coupling the diazo-compound with a naphthol or naphthylamine. The dyes described yield mainly orange and brown shades and are suitable for wool and silk, but a mordanting process is necessary to achieve good fastness. The stability of the dyes to acid and alkali, including boiling fuming nitric acid, is noteworthy. H. H. Hodgson and E. Marsden<sup>22</sup> have investigated the reaction of nitrous acid and *p*-aminomonomethylaniline, the latter having been prepared by reduction of *p*-nitroso- or *p*-nitro-methylaniline with iron, water, and a little ferrous sulphate or ferrous ammonium sulphate. These authors claim that with less than 1 equivalent of nitrous acid, diazotisation occurs without attendant nitrosation. The same authors have also investigated the decomposition of diazobenzene at various pH values.<sup>23</sup>

Distillation of azo-compounds with soda-lime has been shown by E. J. Cross<sup>24</sup> to result, with certain exceptions, in the fission of the azo-group with formation of arylamines. The presence in the azo-compound of a substituent which forms a salt with the alkali appears essential for fission by this method, otherwise the compound behaves as when heated alone. A sulphonic acid group may also be eliminated in the reaction, *e.g.*, sulphanilic acid  $\rightarrow$  dimethylaniline (Methyl Orange, Colour Index No. 142) gives by this treatment aniline, *p*-aminodimethylaniline, *p*-phenylenediamine, and diphenylamine. The main fission of the azo-group under these circumstances would appear to be best explained by hydrolysis.

For the identification of some unsulphonated azo- $\beta$ -naphthol dyes, L. Koch, R. F. Milligan, and S. Zuckerman<sup>25</sup> reduce the dye in a mixture of concentrated hydrochloric acid and dioxan at 80–90° with hydrogen and a platinum catalyst.

Several papers have appeared relating to spectrographic investigations of azo-compounds, with particular reference to the relation between their absorption spectra and chemical constitution. R. A. Donia<sup>26</sup> has investigated the colours and absorption spectra at varying pH of azo-dyes from diazotised 2-aminoanthraquinones containing chlorine, bromine, and/or sulphonic substituents *ortho* to the amino-group.

<sup>21</sup> *Ind. Eng. Chem.*, 1944, **36**, 426; *B.*, 1944, **II**, 307.

<sup>22</sup> *J.C.S.*, 1944, 398; *A.*, 1944, **II**, 331.

<sup>23</sup> *J. Soc. Dyers & Col.*, 1945, **61**, 20; *A.*, 1945, **II**, 113.

<sup>24</sup> *Ibid.*, 74; *B.*, 1945, **II**, 172.

<sup>25</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 755; *C.*, 1945, 105.

<sup>26</sup> *Univ. Pittsburgh Bull.*, 1944, **40**, 56; *A.*, 1945, **II**, 23.



Comparisons of the absorption curves for the azo- and hydrazone forms of certain azo- $\beta$ -naphthol dyes have been made by V. N. Ufimtzev.<sup>27</sup> This author has shown that the difference in structure of the *o*- and *p*-azonaphthol dyes investigated is apparent from the shift of the absorption maxima which occurs on salt formation and ionisation. With *p*-azo-dyes, the shift is towards the long-wave side; with *o*-azo-dyes it is to the opposite side in accordance with the chelate structure. The effect of position isomerism on the absorption spectra of halogen derivatives of benzeneazophenol has been studied by W. R. Brode and La V. E. Cheyney,<sup>28</sup> whilst M. L. Ernsberger and W. R. Brode<sup>29</sup> have reported on the absorption spectra of the copper, nickel, and cobalt compounds of certain simple *o*-hydroxy- and *o*-amino-azo-dyes.

The preparation of the dichloride of 4 : 4'-dinitrostilbene-2 : 2'-disulphonic acid and of 4 : 4'-diacetamidostilbene-2 : 2'-disulphonic acid and the use of these compounds in condensations with *J*-acid (2-amino-5-naphthol-7-sulphonic acid) in pyridine to yield "colourless dyes" for both cotton and wool are described by V. M. Rodionov and F. M. Mandrosova.<sup>30</sup> The structure of a number of substantive azo-dyes and intermediates has been discussed by H. H. Hodgson and E. Marsden from the viewpoint of resonance theory.<sup>31</sup>

M. Mendoza, M. A. T. Rogers, and Imperial Chemical Industries Ltd.<sup>32</sup> have found that 2 : 4-diarylpyrroles, which may carry substituents, *e.g.*, aryl, alkyl, alkylamino, or acylamino, in the 3-position, possess a reactive hydrogen in the 5-position which enables them to react readily with diazonium salts to produce azo-compounds. These authors have described the preparation of certain azo-dyes, including metallisable dyes, for wool and cotton, and certain pigments from this type of coupling component.

#### *Azo-Dyes for Wool.*

Two specifications relate to further investigations by Imperial Chemical Industries on the use of halogenoacyl-*p*-phenylenediamine derivatives as diazo-components for acid wool dyes.<sup>33</sup> They both describe disazo-dyes giving grey, blue, and black shades on wool, fast to wet treatments and to light. In one case the dyes are made by combining a diazotised 4-amino-1-*N*-alkyl- ( $C_1$  to  $C_6$ ) or -cycloalkyl-monochloro- or -bromo-acylanilide in acid medium with *H*-, *K*- or *S*-acids and coupling to the resulting monoazo-compound, under alkaline conditions, any diazotised amine devoid of a halogenoacylamino-group. For example, 4-amino-1-*N*-cyclohexyl- $\alpha$ -chloroacetanilide  $\rightarrow$  (acid) *H*-acid (alkaline)  $\rightarrow$  aniline.<sup>34</sup>

<sup>27</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 351; A., 1944, II, 368.

<sup>28</sup> *J. Org. Chem.*, 1941, **6**, 341; A., 1945, II, 234.

<sup>29</sup> *Ibid.*, 331; A., 1945, II, 234.

<sup>30</sup> *J. Appl. Chem. Russ.*, 1943, **16**, 20; A., 1945, II, 50.

<sup>31</sup> *J. Soc. Dyers & Col.*, 1944, **60**, 210; B., 1944, II, 316.

<sup>32</sup> B.P. 562,762; B., 1944, II, 307.

<sup>33</sup> Cf. *Ann. Repts.*, 1942, **27**, 85; 1943, **28**, 73; 1944, **29**, 78.

<sup>34</sup> B.P. 569,770; B., 1945, II, 298.



In the other case, diazotised amines of the benzene or naphthalene series substituted by at least one halogen or by carboalkoxy,  $\text{CO}_2\text{H}$ ,  $\text{CO}\cdot\text{NH}_2$ ,  $\text{CO}\cdot\text{A}$ , or  $\text{CO}\cdot\text{NHA}$  ( $\text{A}$  = hydrocarbon or substituted hydrocarbon) but devoid of  $\text{NO}_2$ , acidylamino,  $\text{SO}_2$ , and  $\text{SO}_3\text{H}$  groups, are coupled in acid medium with *H*- or *K*-acids and to the resulting mono-azo-compound is coupled under alkaline conditions a halogenoacyl-*p*-phenylenediamine derivative of the type specified above.<sup>35</sup>

A useful addition to the range of mordant dyes is claimed by Brotherton & Co. Ltd.<sup>36</sup> in the monoazo-dye picramic acid  $\rightarrow$  *m*-4-xyleneol (1-hydroxy-2 : 4-dimethylbenzene); this dye gives an olive-green tone when dyed on wool by the afterchrome or single-bath chroming processes in contrast to the olive-brown shade given by the corresponding dye from *p*-cresol under similar dyeing conditions.

P. M. Heertjes and E. A. M. F. Dahmen<sup>37</sup> describe the shade and fastness properties of monoazo-dyes from diazotised 3 : 4-ethylenedioxyaniline (4-aminopyrocatechol ethylene ether) and certain naphthol- or aminonaphthol-sulphonic acids or salicylic acid; they are said to have moderate to good light- and washing-fastness and good rubbing-fastness.

*m*-Tolidine (3 : 3'-dimethylbenzidine) has already been used extensively for making acid disazo-dyes for wool of good milling-fastness.<sup>38</sup> Du Pont de Nemours & Co.<sup>39</sup> have now prepared the 2 : 2'-dichloro-5 : 5'-disulphonic acid thereof, which they use to give both symmetrical and unsymmetrical disazo-dyes of excellent fastness properties. Special emphasis is laid on the dyes from 1-aryl-3-alkyl-5-pyrazolone coupling components; those dyes having not more than two sulphonic groups have good affinity for nylon and have the same fastness properties on that fibre as on wool.

1-Arylamino-7-naphthol-3- or -4-sulphonic acids are used by General Aniline & Film Corporation<sup>40</sup> as coupling components for monoazo- and disazo-dyes (the former by coupling in the 8-position and the latter by coupling in both the 2- and 8-positions) from benzenoid diazo-components. Examples are: 4 : 6-dichloro-2-aminophenol  $\rightarrow$  1-anilino-7-naphthol-4-sulphonic acid, giving greenish-grey shades, fast to fulling, hot-pressing, potting, and light, and *N*-benzoyl-*N*-cyclohexyl-*p*-phenylenediamine  $\rightarrow$  1-anilino-7-naphthol-4-sulphonic acid, giving dark brown shades fast to fulling, potting, and perspiration.

### *Dyes for Cotton.*

Compared with pre-war standards, the amount of patenting on direct cotton dyes coming within this review is very small and no major developments have been recorded.

<sup>35</sup> B.P. 569,771; B., 1945, II, 298.

<sup>36</sup> B.P. 563,772; B., 1944, II, 308.

<sup>37</sup> *Rec. trav. chim.*, 1943, 62, 620; B., 1945, II, 257.

<sup>38</sup> Cf. G.P. 261,047; G.P. 237,440; G.P. 261,555; G.P. 235,948; G.P. 238,549; B.P. 481,477.

<sup>39</sup> B.P. 569,080; B., 1945, II, 265.

<sup>40</sup> U.S.P. 2,191,823; B., 1945, II, 256.



Interest in dyes capable of after-treatment by formaldehyde or development with diazo-compounds continues, and some attention has again been paid to dyes capable of being diazotised on the fibre and developed with suitable coupling components. The objective in most of these cases is increased washing-fastness rather than novelty in shade, and the application in several cases appears to be specially directed towards the dyeing of viscose. Resorcinol is the final coupling component most favoured for dyes for formaldehyde after-treatment.

Du Pont de Nemours & Co. have described blue and blue-violet straight-chain trisazo-dyes of the type A (benzenoid)  $\rightarrow$  M (benzenoid or naphthalenoid)  $\rightarrow$  *N*-(4'-amino-3'-sulpho- or -carboxy-phenyl)-*J*-acid  $\rightarrow$  resorcinol<sup>41</sup> and red shade dyes of the type A (benzenoid)  $\rightarrow$  M (benzenoid)  $\rightarrow$  1- or 2-aminonaphtholsulphonic acid (hydroxy at 5, 6, 7, or 8 positions) in which the amino-group is substituted by aminobenzoyl or aminobenzamidobenzoyl  $\rightarrow$  resorcinol, an example of the latter type being sulphanilic acid  $\rightarrow$  aniline  $\rightarrow$  *p*-aminobenzoyl-*J*-acid  $\rightarrow$  resorcinol.<sup>42</sup> Tetrakisazo-dyes disclosed by Society of Chemical Industry in Basle<sup>43</sup> which can be developed on the fibre with a diazo-compound (with alteration in shade and marked improvement in washing-fastness) or after-treated on the fibre with formaldehyde (with little shade change but improvement in washing-fastness) and which yield shades varying from red-violet to grey-violet, dark brown, and olive-green are of the pattern: resorcinol or *m*-aminophenol  $\leftarrow$  diamine (other than *ortho*) of the benzene or naphthalene series  $\rightarrow$  *J*-, *M*-, or Gamma-acid  $\rightarrow$   $\alpha$ -naphthylamine, Cleve's acid, or a 2-alkoxy-Cleve's acid  $\rightarrow$  resorcinol or *m*-aminophenol. For example, the dye resorcinol  $\leftarrow$  *p*-phenylenediamine  $\rightarrow$  Gamma-acid  $\rightarrow$   $\alpha$ -naphthylamine  $\rightarrow$  resorcinol yields black shades on cotton when after-treated with diazo-*p*-nitrobenzene.

In another specification<sup>44</sup> the same firm restrict the diamine in the above pattern to one of the benzene series, replace the *J*-, *M*-, or Gamma-acid by a benzenoid middle component, and the  $\alpha$ -naphthylamine etc. by *J*-, *M*-, or Gamma-acid; the derived dyes dye cotton and viscose in red or red-violet to dark blue-green, olive-green, black, and brown shades. The use of *m*-phenylenediamine as an end component for dis- and tris-azo-dyes followed by acylation of one or both amino-groups by a nitrobenzoyl halide and reduction of the nitro-group(s) is described by Du Pont de Nemours & Co.<sup>45</sup> The resulting dyes contain two diazotisable amino-groups and they may be diazotised on the fibre and developed with suitable coupling components, or the acylation and reduction processes may be repeated in substance before such after-treatments are given. The same company have described further dyes for which

<sup>41</sup> U.S.P. 2,322,750; B., 1945, II, 209.

<sup>42</sup> U.S.P. 2,322,746; B., 1945, II, 209.

<sup>43</sup> B.P. 564,024; B., 1944, II, 350.

<sup>44</sup> B.P. 564,258; B., 1944, II, 350.

<sup>45</sup> U.S.P. 2,182,347-8; B., 1945, II, 54.



2-aminobenzidine is used as end component (*E*) to provide the diazotisable amino-group for development. Typical examples are  $E \leftarrow$  benzidine  $\rightarrow$  1-sulphophenyl-3-methyl-5-pyrazolone and 2-naphthylamine-4 : 8-disulphonic acid  $\rightarrow$  *m*-toluidine  $\rightarrow$  *m*-toluidine  $\rightarrow$  *E*, which give orange-brown and maroon-brown shades respectively on diazotisation and development with  $\beta$ -naphthol.<sup>46</sup>

Du Pont de Nemours & Co. also describe tetrakisazo-dyes for tetrazotisation and development on the fibre with  $\beta$ -naphthol or 1-phenyl-3-methyl-5-pyrazolone, and of the pattern  $D \rightleftharpoons (1\text{-aminoaryl-5-pyrazolone})_2 \rightleftharpoons (\text{arylamine})_2$ , *D* being a diamine  $\text{NH}_2\cdot\text{Ar}\cdot\text{X}\cdot\text{Ar}'\cdot\text{NH}_2$ ; where *X* =  $\text{CH}:\text{CH}$ ,  $[\text{CH}_2]_2$ ,  $\text{CH}_2$ , *O*, *CO*, *CO*·*NH*, etc. The arylamino final coupling component may be 1 : 6- or 1 : 7-Cleve's acid<sup>47</sup> or a 1-aminoaryl-5-pyrazolone.<sup>48</sup> For example, benzidine-3 : 3'-disulphonic acid  $\rightleftharpoons [1\text{-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid}]_2 \rightleftharpoons (1\text{-phenyl-3-methyl-5-pyrazolone})_2$  gives yellow shades.

There have been few developments to record during the period under review in the field of metallisable dyes for cotton. The trend of developments in the past few years, to judge by published patent specifications, has been in the direction of after-coppering dyes, and the types of constitution employed have suggested that attempts were being made by certain dye-makers to combine the improved light-fastness usually conferred by the introduction of co-ordinated copper into a suitable cotton dye molecule with a higher degree of washing-fastness than is possessed by many copper-containing direct dyes.

Geigy A.-G.<sup>49</sup> have claimed the manufacture of copper complexes of disazo-dyes obtained by coupling the urea of *J*-acid with two different diazo-components, one being a diazotised anthranilic acid (devoid of aroylamino-groups) and the other 6-chloro-2-aminophenol-4-sulphonic acid. Alternatively, a triazine residue may replace the *CO* group in linking the two molecules of *J*-acid. Bluish-red shade dyes are obtained which are said to have advantages in respect of exhaustion, washing- and water-fastness, and, in some cases, light-fastness over similar known dyes.

2-Naphthol-4-sulphonic acid is used as coupling component by Sandoz Ltd.<sup>50</sup> in the preparation of some brown shade chrome-printing monoazo-dyes of good fastness to soaping and chlorine, the diazo-components employed being *p*-aminophenol-*o*-carboxylic acid or a nuclearly substituted derivative thereof.

A method for producing azo-derivatives of cellulose is described in a paper by P. A. Solodkov.<sup>51</sup>

<sup>46</sup> U.S.P. 2,178,757; B., 1944, II, 307. Cf. U.S.P. 2,164,524; B., 1943, II, 279.

<sup>47</sup> U.S.P. 2,191,800; B., 1945, II, 265.

<sup>48</sup> U.S.P. 2,191,801; B., 1945, II, 265.

<sup>49</sup> B.P. 562,641; B., 1944, II, 308.

<sup>50</sup> B.P. 567,217; B., 1945, II, 173.

<sup>51</sup> J. Appl. Chem. Russ., 1943, 16, 351; B., 1945, II, 109.



*Azoic Dyes.*

The continued search for "stabilisers" for triazens for printing pastes represents the most conspicuous feature of the patenting activity in this field. Few new azoic bases or coupling components have been disclosed.

P. Petitcolos and J. Frenkiel<sup>52</sup> describe the manufacture of 2-hydroxyalkylamino-5-sulphobenzoic acids by condensing a hydroxyalkylamine, *e.g.*,  $\beta$ -hydroxyethylamine, and a salt of 2-chloro-5-sulphobenzoic acid; the products are said to be useful for the preparation of diazoimino-compounds capable of being hydrolysed by organic acids.

Secondary arylamines carrying alkoxy- or aralkyloxy-groups, which in turn carry water-solubilising groups, are used by the National Aniline & Chemical Co.<sup>53</sup> to stabilise diazonium salts of water-insoluble arylamines; these compounds, of which 1-methylamino-2:4-di-( $\beta$ -sulphatoethoxy)benzene and 1-methylamino-4-disulphobenzyloxybenzene are examples, contain the substituent groups in positions calculated to inhibit coupling.

The American Cyanamid Co. employ guanidyl-sulphonic and -carboxylic acids and their alkali and ammonium salts, *e.g.*, the salt  $\text{NH}_2\cdot\text{C}(\text{:NH})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$ , as stabilisers for triazens,<sup>54</sup> and claim the use of such stabilised preparations in making printing mixtures.<sup>55</sup> Guanylurea and derivatives thereof are used by the same firm as stabilisers for diazoimino-compounds; for example, diazotised *p*-toluidine is combined with the compound  $\text{NH}_2\cdot\text{C}(\text{:NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , the product mixed with an arylamide of 2-hydroxy-3-naphthoic acid, and made into a printing paste.<sup>56</sup> Sulphamic acid ( $\text{NH}_2\cdot\text{SO}_3\text{H}$ ) or its salts are used by Allied Chemical & Dye Corporation to stabilise diazonium double salts (*e.g.*, zinc double salt) of *p*-chloro-*o*-nitroaniline, either dry or in solution.

To reduce the speed of decomposition of the diazo-compound present in a printing paste in the form of a stabilised salt, especially diazonium metal halide complexes, the Du Pont Co.<sup>57</sup> add unsaturated aliphatic carboxylic acids or water-soluble metal salts thereof; the acid may be mixed with the arylamine before diazotisation.

Stable, water-soluble compositions are prepared by General Aniline & Film Corporation<sup>58</sup> by mixing the usual azoic coupling components, *e.g.*, phenols, naphthols, heterocyclic hydroxy-compounds or their carboxy-arylamides, with aqueous sodium or potassium silicates, borates, stannates, or phosphates, or drying down with caustic soda and sodium silicate.

<sup>52</sup> U.S.P. 2,316,809; B., 1945, II, 101.

<sup>53</sup> U.S.P. 2,190,841; B., 1945, II, 237.

<sup>54</sup> U.S.P. 2,185,152 and 2,185,154; B., 1945, II, 50.

<sup>55</sup> U.S.P. 2,185,153; B., 1945, II, 50.

<sup>56</sup> U.S.P. 2,314,652; B., 1944, II, 350.

<sup>57</sup> U.S.P. 2,314,196; B., 1945, II, 8.

<sup>58</sup> U.S.P. 2,319,265; B., 1945, II, 173.

<sup>59</sup> U.S.P. 2,190,746-7; B., 1945, II, 237.



Acylaceto-derivatives of monoacylbenzidines or nuclear derivatives thereof, excepting those containing groups giving solubility in water, are employed by the Du Pont Co.<sup>60</sup> as coupling components for diazo-compounds preferably formed in the fibre by scission of a triazen with acid. Yellow prints are obtained from the combination 4-acetamido-4'-acetoacetamido-3 : 3'-dimethyldiphenyl  $\rightarrow$  the diazo-compound regenerated from the triazen 4-chloro-2-anisidine  $\rightarrow$  pipercolinic acid by acid steaming.

The Du Pont Co.<sup>61</sup> also describe the preparation of diazotisable amino-azo-compounds by coupling diazotised mono- or di-amines of the benzene, naphthalene, anthracene, carbazole, diphenyl, or azobenzene series, devoid of groups imparting water-solubility, under alkaline conditions with a variety of aminonaphthols. Their diazonium chlorides or the zinc double salts thereof are stable in solution or can be isolated, and dried,<sup>62</sup> and used in the usual way as ice colour components. For example, brown shades are obtained by padding cotton with the *o*-anisidide of 2-hydroxy-3-naphthoic acid and coupling with the diazo-compounds of *m*-xylydine or 1 : 5-, 1 : 6-, or 1 : 7-aminonaphthols.<sup>63</sup>

#### *Dyes for Acetate Rayon.*

Recent research on azo-dyes for acetate rayon has proceeded towards two main objectives, one being an extension of the shade range and improvement in the fastness properties of water-insoluble dyes for application by dispersion techniques, the other being the wider application of known methods of making water-soluble dyes for this fibre and discovery of suitable new solubilising groups. There is a tendency nowadays, where the chemical structures involved permit, for patentees to provide for both types of dye in one and the same patent specification. However, the present position technically is such that, whilst many dye manufacturers have ranges of dispersed-type dyes for acetate rayon, no other manufacturer has introduced a range of new water-soluble dyes to compete with the Solacet dyestuffs of Imperial Chemical Industries.<sup>64</sup>

It is noteworthy that many of the patent specifications for dyes for acetate rayon also allege that they are suitable for colouring nylon.

Sulphochloroacetic esters of *N*-hydroxyalkylarylamines of the benzene series are used by Society of Chemical Industry in Basle<sup>65</sup> as coupling components for new water-soluble dyes, an example being the esterified blue dye from 2 : 4-dinitro-6-cyanoaniline  $\rightarrow$  *N*-methyl-*N*- $\beta$ -hydroxy-ethyl-*m*-toluidine. Eastman Kodak Co.<sup>66</sup> use components, diazo or coupling, which carry hydroxyalkoxy-substituents the hydroxyl group

<sup>60</sup> U.S.P. 2,193,553; B., 1945, II, 298.

<sup>61</sup> U.S.P. 2,193,996; B., 1945, II, 298.

<sup>62</sup> U.S.P. 2,193,998; B., 1945, II, 298.

<sup>63</sup> U.S.P. 2,193,997; B., 1945, II, 298.

<sup>64</sup> *Silk J. & Rayon World*, 1936, 12, 47.

<sup>65</sup> B.P. 565,697; B., 1945, II, 75.

<sup>66</sup> U.S.P. 2,183,998; B., 1944, II, 349.



of which is esterified by phosphoric acid or thiophosphoric acid, *e.g.*,  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{PO}_4\text{H}_2 \rightarrow 5:5\text{-dimethylcyclohexane-1:3-dione}$  for greenish-yellow shades. 5-Alkyl- or 5:5-dialkyl-cyclohexane-1:3-diones are also used by the same firm<sup>67</sup> as coupling components for certain dispersible monoazo-dyes claimed for colouring acetate rayon, the diazo-components for these being a 4-halogeno- or -nitro-2-alkylaniline, a 4-halogeno-, -alkyl-, or -alkoxy-2-nitroaniline or a 3-halogeno- or -nitro-4-aminophenyl alkyl ketone.

Patents continue to appear relating to highly substituted derivatives of the monoazo-pattern  $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NRR}'\text{-}p$ , in which Ar is phenyl usually carrying a *p*-nitro-group and at least one of R and R' is a hydroxy-alkyl group. The nitrogen of the coupling component which determines position of coupling can also form part of a heterocyclic ring system.<sup>68</sup> The main objectives here would still seem to be the extension of the shade range towards the green end of the spectrum, and the provision of dyes of good resistance to the "fading" action of burnt gas fumes. In addition to diazo-components which have already been widely used in this type of dyes, such as *p*-nitroaniline, 2-halogeno- and 2:6-dihalogeno-*p*-nitroanilines, 2:4-dinitroaniline, and 6-cyano- or -halogeno- or -sulphonamido- (including *N*-substituted sulphonamido-)derivatives thereof, there may be mentioned related amines having a CO·Alkyl group<sup>69</sup> or a SO<sub>2</sub>X group (X = alkyl, carboxyalkyl, or alkylcarboxyl-amino)<sup>70</sup> in *ortho* position to the diazotisable amino-group (for rubine to blue shades), 5:6-dichloro-4-nitroaniline (for violet shades),<sup>71</sup> and 5-nitro-3-methoxyaniline (for orange-yellow shades).<sup>72</sup>

New coupling components selected by the same firm for this broad constitutional pattern are 1:2:3:4-tetrahydrocinnolines, which couple at the 6-position (rubine, violet, and blue shades),<sup>73</sup> 1-alkyl- or -hydroxy-alkyl-2-alkyl-1:2:3:4-tetrahydroquinolines or -benzmorpholines (for rubine to violet shades),<sup>74</sup> 5- or -7-acetamido-*N*-alkyl- or -hydroxyalkyl-2- or -3-alkylbenzmorpholines and corresponding benzdihydrothiazines and benzdihydrothiazones (blue shades),<sup>75</sup> and  $\alpha$ -naphthylamines in which one hydrogen of the amino-group is replaced by a  $\beta\gamma$ -dihydroxypropyl group, one OH being esterified, *e.g.*, by acetyl, and the other left free or replaced by alkyl, esterified hydroxyalkyl, cycloalkyl, etc. (red and violet shades).<sup>76</sup>

Derivatives of 1-amino-5-naphthol in which one hydrogen of the amino-group is replaced by an alkyl group carrying a tetrahydrofuryl

<sup>67</sup> U.S.P. 2,183,997; B., 1944, II, 349.

<sup>68</sup> Cf. *Ann. Repts.*, 1937, 22, 129; 1939, 24, 116.

<sup>69</sup> Eastman Kodak Co., U.S.P. 2,317,365; B., 1945, II, 104.

<sup>70</sup> *Idem*, U.S.P. 2,323,315; B., 1945, II, 265.

<sup>71</sup> *Idem*, U.S.P. 2,311,033; B., 1944, II, 307.

<sup>72</sup> *Idem*, U.S.P. 2,180,012; B., 1944, II, 307.

<sup>73</sup> U.S.P. 2,322,925; B., 1945, II, 209.

<sup>74</sup> U.S.P. 2,323,315; B., 1945, II, 265.

<sup>75</sup> U.S.P. 2,319,217; B., 1945, II, 173.

<sup>76</sup> U.S.P. 2,323,314; B., 1945, II, 265.



radical at position 2 (= R), and the other is optionally replaced by aryl of the benzene series, alkyl, alkoxy, or R and the hydroxyl group may be esterified, are used as coupling components for diazotised benzenoid arylamines or aminobenzthiazoles. For example, the combination 6-chloro-2 : 4-dinitroaniline  $\rightarrow$  1-*N*-tetrahydrofurfurylmethylamino-5-naphthol yields blue-green shades and 2-amino-6-methoxybenzthiazole  $\rightarrow$  1-*N*-sulphatoethyl-*N*-tetrahydrofurfurylmethylamino-5-naphthol blue shades.<sup>77</sup> Dispersed monoazo-dyes from sulphazone coupling components are used to produce yellow shades; for example, *o*-anisidine  $\rightarrow$  7-nitro-4-methylsulphazone (greenish-yellow).<sup>78</sup> Secondary disazo-dyes yielding yellow and orange shades, and closely related to those described by British Celanese in B.P. 398,842, are obtained by Du Pont de Nemours & Co.<sup>79</sup> by coupling certain diazotised aminoarylsulphonamides  $p$ -NH<sub>2</sub>·Ar·SO<sub>2</sub>·NHR, where Ar is of the benzene or naphthalene series and R is H or certain hydroxyalkyl groups, with a benzenoid or naphthalenoid middle component or a 1-aminophenyl-3-methyl-5-pyrazolone, rediazotising, and coupling with a phenol.

### *Lakes and Pigments.*

Metallised monoazo-pigments of good light-fastness are obtained by Du Pont de Nemours & Co.<sup>80</sup> by coupling diazotised arylamines, devoid of a hydroxyl group *ortho* to the amino-group and of carboxyl and sulphonic groups, with 2-hydroxy-3-naphthoic acid or derivatives thereof substituted in the ring not containing the hydroxyl group, and treating the resulting pigments with salts of certain metals, *e.g.*, nickel, cobalt, copper, iron etc., so that 2 mols. of pigment combine with 2 atoms of metal, at least one of the metal atoms being nickel or cobalt. Advantages of shade and tinctorial strength which may accrue from the preparation *in situ* of mixtures of certain pigments have been referred to in previous reviews.<sup>81</sup> The Du Pont Co. now claim to get greater tinctorial strength from a mixture of the calcium lakes of 6-chloro-*p*-toluidine-3-sulphonic acid (*A*)  $\rightarrow$  2-hydroxy-3-naphthoic acid (*E*) and another isomeric pigment, *e.g.*, 3-chloro-*o*-toluidine-5-sulphonic acid  $\rightarrow$  *E* than from *A*  $\rightarrow$  *E* itself.<sup>82</sup>

## ANTHRAQUINONE DYES.

### *Intermediates.*

A. T. Peters and F. M. Rowe<sup>83</sup> have investigated in more detail the preparation of 2-alkylanthraquinones by Friedel-Crafts methods, where the alkyl group consists of isopropyl, *n*- and *tert.*-butyl, *n*-amyl, -heptyl, -octyl, and -dodecyl. The ring-closure with sulphuric acid or oleum

<sup>77</sup> Eastman Kodak Co., U.S.P. 2,183,999; B., 1944, II, 349.

<sup>78</sup> *Idem*, U.S.P. 2,186,629; B., 1945, II, 81.

<sup>79</sup> U.S.P. 2,317,387; B., 1945, II, 104.

<sup>80</sup> B.P. 565,951; B., 1945, II, 88.

<sup>81</sup> *Ann. Repts.*, 1940, 25, 118; 1941, 26, 94; 1942, 27, 91; 1943, 28, 78; 1944, 29, 83.

<sup>82</sup> U.S.P. 2,189,806; B., 1945, II, 173.

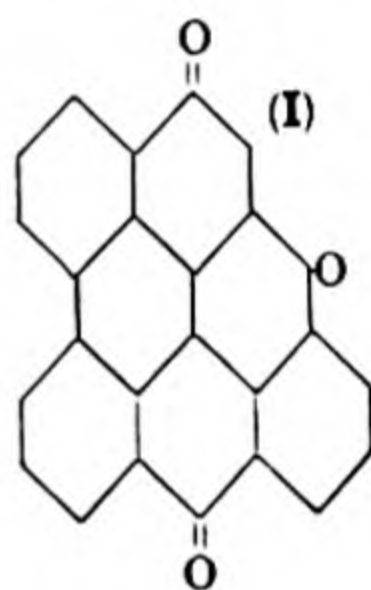
<sup>83</sup> *J.C.S.*, 1945, 181; A., 1945, II, 307.



gives no 2-alkylanthraquinones in the last four cases, and with the other three, gives 33% of 2-isopropyl- (where sulphonation lowers the yield), 73% of 2-*n*-butyl-, and 75% of 3-*tert*.-butyl-anthraquinone.

E. I. Du Pont de Nemours & Co. have two patents describing a range of intermediates characterised by a cyano-group in the 5- or 8-position, in addition to the usual other groups needed for wool or acetate rayon dyes, *i.e.*, amino (or its derivatives) at 1, bromine at 4, and bromine, a sulphonyl-group, or hydrogen at 2. These are prepared and converted into other derivatives by the usual methods.<sup>84</sup> 6-Chloro-1-aminoanthraquinone is described by the same firm, prepared by means of the toluene-sulphonamide reaction from 1 : 6-dichloroanthraquinone.<sup>85</sup> The oxidation of leuco-1-amino-4-hydroxy- or -1 : 4-diamino-anthraquinone or their alkyl derivatives, often carried out by means of organic nitro-compounds, is claimed by the National Aniline & Chemical Co.<sup>86</sup> to give improved results in some cases by employing an aromatic nitroso-compound. The Allied Chemical & Dye Corporation<sup>87</sup> remove the 2-sulphonic group from 1-amino-4-*p*-aroylaminoanthraquinone-2-sulphonic acid by means of furfuraldehyde and alkali.

L. Clar, in a patent assigned to E. I. Du Pont de Nemours & Co.,<sup>88</sup> shows how 1- $\beta$ -naphthoxyanthraquinone may be dehydrogenated by aluminium chloride fusion to 12 : Bz-1-oxido-1 : 2-benzperylene, which can be oxidised to its 3 : 10-quinone (I), which is a brown vat dye.



#### Wool Dyes.

Polyhydroxyalkylamine salts of the well-known anthraquinone acid wool dyes (*e.g.*, Sky Blue, Cyanine Green, and Rubinol) are prepared by E. I. Du Pont de Nemours & Co.,<sup>89</sup> presumably giving better solubility. Level-dyeing properties are claimed by the same firm for the 5- or 6-hydroxyalkoxy-derivatives of 1-amino-4-arylaminoanthraquinone-2-sulphonic acids, without significant alteration in shade of the parent dye. Imperial Chemical Industries<sup>90</sup> use *trans*-2-benzylcyclohexylamine as the arylamine in a 1 : 4-diarylaminoanthraquinone and sulphonate to give a green-blue dye, similar products being obtained with related amines such as 2-benzylcyclopentylamine, 2-*p*-methoxybenzyl- and 2-*o*-chlorobenzyl-cyclohexylamine.

E. I. Du Pont de Nemours & Co.<sup>91</sup> prepare, as grey wool dyes, sulphonated 8-amino- or -alkyl-, -aralkyl-, or -aryl-amino-4- or -5-acylamido-

<sup>84</sup> U.S.P. 2,180,336-7; B., 1944, II, 347.

<sup>85</sup> U.S.P. 2,181,034; B., 1944, II, 347.

<sup>86</sup> U.S.P. 2,185,709; B., 1945, II, 10.

<sup>87</sup> U.S.P. 2,321,767; B., 1945, II, 208.

<sup>88</sup> U.S.P. 2,179,920; B., 1944, II, 348.

<sup>89</sup> (a) U.S.P. 2,314,356; B., 1944, II, 350. (b) U.S.P. 2,179,217; B., 1944, II, 350.

<sup>90</sup> B.P. 564,859; B., 1945, II, 9.

<sup>91</sup> U.S.P. 2,318,174; B., 1945, II, 173.



anthraquinone-1 : 2 : 2' : 1'-naphthacarbazoles. Thus 5-chloro-4-amino-1-benzamidoanthraquinone is condensed with  $\beta$ -naphthylamine and the resulting 5-naphthylamino-compound sulphonated and cyclised in one operation with oleum.

*Dyes for Cellulose Acetate Rayon.*

The Eastman Kodak Co.<sup>92</sup> prepare 1-alkylamino-4- $\beta$ -aminoanilinoethylaminoanthraquinones, optionally substituted by hydroxyl, amino, or alkylamino at 5 and/or 8; thus 4- $\beta$ -*p*-aminoanilinoethylaminoanthraquinone having a 1-hydroxyl group gives purple shades; 1-morpholino- and 1-tetrahydrofurfurylamino-, blue; 1 : 5-dimethylamino-, blue-green. The same firm, by condensing leucoquinizarin with ethanolamine and methyl  $\beta$ -amino-*n*-butyrate in equimolecular amounts and oxidising the product, obtain methyl  $\beta$ -(1- $\beta'$ -hydroxyethylaminoanthraquinonyl-4-amino)butyrate, which dyes blue shades.<sup>93</sup>

The same firm describe a range of dyes solubilised by means of a sulphoalkylamino-group, the alkyl being of two carbons at least.<sup>94</sup> Again, the same firm describe a series of 1-(2- $\omega$ -furyl)alkylamino- or 1-(2-tetrahydrofuryl)alkylamino-anthraquinones, in which the 5-position of the furan ring may have a group  $\cdot[\text{CH}_2]_n\cdot\text{OH}$  or  $\cdot[\text{CH}_2]_n\cdot\text{NH}_2$ . Again, the tetrahydrofurylalkylaminoanthraquinones of this type may have hydroxyl, alkoxyl, amino-, or tetrahydrofurylalkylamino-groups in the 5- and/or 8-positions of the anthraquinone molecule.<sup>95</sup>

*Vat Dyes.*

2-Chloroanthraquinone-6-carboxyl chloride has been used by E. I. Du Pont de Nemours & Co.<sup>96</sup> as an acylating agent; thus 6-chloro-1-aminoanthraquinone yields a yellow vat dye with this reagent, changed to orange-red by further condensation with 1-aminoanthraquinone, or violet with 1-amino-4-benzamidoanthraquinone, and corresponding shades with other variants.

Imperial Chemical Industries<sup>97</sup> introduce two different alkane- or phenylalkane-sulphonylbenzoyl groups into 1 : 4-diaminoanthraquinone, obtaining scarlet to red vat dyes of good kier-boiling-fastness.

The Du Pont Co.<sup>98</sup> describe 1 : 4-diaroylamidoanthraquinone-6-carboxylamidoanthraquinones, particularly derivatives of this type of acid with 1-amino-4-benzamido- and 1 : 4-diamino-anthraquinones, which are red to red-brown cold-dyeing vat dyes.

General Aniline & Film Corporation<sup>99</sup> describe leuco-sulphuric esters of yellow to brown vat dyes of the monoazo-type

<sup>92</sup> U.S.P. 2,311,065; B., 1944, II, 308.

<sup>93</sup> U.S.P. 2,319,043; B., 1945, II, 104.

<sup>94</sup> U.S.P. 2,188,369; B., 1945, II, 174.

<sup>95</sup> U.S.P. 2,191,029-030; B., 1945, II, 238.

<sup>96</sup> U.S.P. 2,181,048; B., 1944, II, 347.

<sup>97</sup> B.P. 568,933; B., 1945, II, 238.

<sup>98</sup> U.S.P. 2,179,552; B., 1944, II, 350.

<sup>99</sup> U.S.P. 2,316,758; B., 1945, II, 105.



$A \cdot N_2 \cdot CHAc \cdot CO \cdot NH \cdot C_6H_4 \cdot CF_3$ , where *A* is anthraquinone; they are produced by diazotising 1-aminoanthraquinone and coupling with trifluoromethylacetoacetanilides such as acetoacet-*m*-trifluoromethylanilide or acetoacet-2-ethanesulphonyl-5-trifluoromethylanilide.

Among carbazole types of vat dyes, E. I. Du Pont de Nemours & Co.<sup>100</sup> condense 5-amino-2 : 1(*S*)-anthraquinonethioxanthone with 1-chloro-4- or -8-benzamidoanthraquinone and cyclise by aluminium chloride fusion in pyridine or nitrobenzene and subsequent oxidation; the dyes are orange to red in shade, are fast to bleaching, and have printing properties. Imperial Chemical Industries<sup>101</sup> obtain brown to grey dyes of very good light-, soda-boil-, and bleach-fastness by condensing a 3- to 8-halogeno-arylamidoanthraquinone-2 : 1(*N*)-acridone with a 4-, 5-, or 8-amino-1-arylaminoanthraquinonecarbazole. Alternatively, a 3- to 8-aminoanthraquinone-2 : 1(*N*)-acridone may be condensed with a 4-, 5-, or 8-carboxyarylamino-1-arylaminoanthraquinonecarbazole or its amide-forming derivatives, or with a similar compound having halogen in place of carboxyl. Or, again, a 3- to 8-carboxyarylaminoanthraquinone-2 : 1(*N*)-acridone may be condensed with a 4-, 5-, or 8-amino-1-arylaminoanthraquinonecarbazole.

The Du Pont Co.<sup>102</sup> describe 1 : 4-diamino-, -diarylamido-, or diarylsulphonamido-derivatives of the well-known 6 : 2'-anthraquinonylanthraquinone-2(*N*) : 1-thiazole; thus the sodium salt of 2-amino-1-thiolanthraquinone is condensed with 1 : 4-dichloroanthraquinone-6-carboxyl chloride, and the product diaminated by means of *p*-toluenesulphonamide and hydrolysis, and benzoylated to a red-brown vat dye. Allied Chemical & Dye Corporation<sup>103</sup> prepare carbazoles from trianthrimides having an acridone grouping present in one nucleus, *e.g.*, 1(*N*) : 2-benzacridonyl-5 : 5' : 1' : 1''-, -5 : 8' : 1' : 1''-, -8 : 5' : 1' : 1''-, and -8 : 8' : 1' : 1''-trianthrimides; the dyes are browns of high fastness properties. The first-mentioned intermediate is prepared by condensing 1 mol. each of 1-aminoanthraquinone and 5-amino-1 : 2-anthraquinoneacridone with 1 : 5-dichloroanthraquinone and the others by similar methods.

#### *Dibenzanthrones.*

The Du Pont Co.<sup>104</sup> describe a purification method specially applicable to dibenzanthrone and isodibenzanthrone. The crude compound is stirred with sulphuric acid of 94.5—97.5% concentration until converted into large crystals; the acid is then diluted to not less than 90% and filtered off.

The same firm have greatly extended their study of the reduction products of 16 : 17-dihydroxydibenzanthrone.<sup>105</sup> A stable leuco-com-

<sup>100</sup> B.P. 561,754; B., 1944, II, 308.

<sup>101</sup> B.P. 566,872; B., 1945, II, 173.

<sup>102</sup> U.S.P. 2,179,551; B., 1944, II, 350.

<sup>103</sup> U.S.P. 2,315,537; B., 1945, II, 75.

<sup>104</sup> U.S.P. 2,180,299; B., 1944, II, 351.

<sup>105</sup> U.S.P. 2,183,625; B., 1945, II, 10.



pound can be isolated as the monosodium salt from a hydrosulphite vat by reducing the pH to 9—12 at 60—90° until precipitation is complete; this compound, dissolving in sulphuric acid with a blue colour, is unchanged on precipitation, even after heating at 100°. A number of derivatives of this and of normal leuco-dibenzanthrones are described; for instance, it esterifies normally to the disulphuric ester.<sup>106</sup> The  $\beta$ -hydroxyethyl and homologous ethers are obtained from the stable leuco-compound of 16 : 17-dimethoxydibenzanthrone and its *iso*-analogue, the acid sulphates of which dye cotton red, regenerated to the parent shades by acid.<sup>107</sup> Esters of the leuco-compounds with fatty acids of not less than eight carbon atoms, especially the dilaurates, can be prepared and are useful oil-soluble fluorescent colours.<sup>108</sup>

### *Benzanthroneacridines.*

E. I. Du Pont de Nemours & Co.<sup>109</sup> obtain olive to grey vat dyes by condensing an  $\alpha$ -halogeno- or 9-bromo-3 : 1'-anthraquinonylamino-benzanthrone, or their substituted derivatives, with a 1-aminoanthraquinone-2-phenylazomethine followed by alkali fusion to close the acridine ring in the 4 : 2'-positions. Again, olive dyes are obtained by condensing 3 : 9-dibromobenzanthrone (2 mols.) with a 1 : 4-, 1 : 5-, or 1 : 8-diaminoanthraquinone, then with 1-aminoanthraquinone, and fusing with alkali; the products probably contain both an acridine and a carbazole ring.<sup>110</sup>

General Aniline & Film Corporation<sup>111</sup> describe another type of vat dye of large molecular size produced by condensing a dihalogenoanthanthrone with 1 mol. each of aminoanthraquinone and an aminoaroyl-aminoanthraquinone; the resulting dyes are blue-grey in shade.

### PTHALOCYANINES.

N. H. Haddock<sup>112</sup> has made a useful comprehensive review of this field.

American Cyanamid Co.<sup>113</sup> describe the preparation of copper phthalocyanine from phthalonitrile, which may contain phthalamide, in presence of a cupric salt and ammonia in an inert diluent at 180—220°.

Imperial Chemical Industries continue their studies of sodium sulphide-soluble phthalocyanine derivatives by heating a phthalocyaninesulphonyl chloride with a thiol such as benzylthiol, 2-thiolbenzthiazole, toluene-*p*-thiol,<sup>114</sup> or thioamides<sup>115</sup>; the dyes are mainly green. The same firm<sup>116</sup>

<sup>106</sup> U.S.P. 2,188,320; B., 1945, II, 209.

<sup>107</sup> U.S.P. 2,183,626-7; 2,183,629-30; B., 1945, II, 209.

<sup>108</sup> U.S.P. 2,183,628; B., 1945, II, 209.

<sup>109</sup> U.S.P. 2,312,401, 2,312,462; B., 1944, II, 308.

<sup>110</sup> U.S.P. 2,188,537-8; B., 1945, II, 174.

<sup>111</sup> U.S.P. 2,320,694; B., 1945, II, 173.

<sup>112</sup> *J. Soc. Dyers & Col.*, 1945, 61, 68; B., 1945, II, 173.

<sup>113</sup> B.P. 559,247; B., 1945, II, 10. U.S.P. 2,318,783, 2,318,787; B., 1945, II, 105.

<sup>114</sup> B.P. 566,740; B., 1945, II, 105.

<sup>115</sup> B.P. 566,741; B., 1945, II, 105.

<sup>116</sup> B.P. 569,200; B., 1945, II, 299.



describe a further series of diazonium salts where the nitrogen is in a benzene ring attached to the phthalocyanine nucleus by  $\cdot\text{CO}\cdot$ ,  $\cdot\text{O}\cdot$ , or  $\cdot\text{SO}_2\cdot$ . The products are prepared by submitting anhydrides, amides, or imides of the substituted phthalic acids  $x : 1 : 2\text{-(NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{X)C}_6\text{H}_3(\text{CO}_2\text{H})_2$  ( $\text{X} = \cdot\text{CO}\cdot$ ,  $\cdot\text{O}\cdot$ , or  $\cdot\text{SO}_2\cdot$ ) to the phthalocyanine process in presence of urea and a metal salt; the substituted phthalocyanine is then reduced and diazotised. \* The diazonium salts are more stable than those in which the amino-group is directly attached to the phthalocyanine nucleus. The copper tetra-4-(*p*-aminobenzoyl)phthalocyanine is an example of such amines.

#### PRODUCTS DERIVED FROM 2 : 4-DIARYLPYRROLES.

Eight patents by Imperial Chemical Industries are noted,<sup>117</sup> dealing with a full development of the chemical reactions of 2 : 4-diarylpyrroles of which the first were described last year.<sup>118</sup> The products in general are either methines or azamethines and give rise to a series of dyes which may be of the pigment, basic, or acid wool classes. The basic reaction consists in treating 2 : 4-diarylpyrroles, which may have alkyl, aryl, or acylamino-groups at 3, either with reagents such as ethyl chloroformate, benzotrichloride, or the like capable of linking two molecules by a  $\text{:CR}\cdot$  link ( $\text{R}$  being hydrogen, alkyl, aralkyl, or aryl), or with a 2 : 4-diarylpyrrole having a  $\cdot\text{CO}\cdot$  group at 5; the products are tetra-aryldipyrromethines.<sup>117a</sup> As an example of a dye, 2 : 4-diphenylpyrroledisulphonic acid may be condensed with 5-formyl-2 : 4-diphenylpyrrole, the resulting wool dye being reddish-blue. The dyes of this type, or the corresponding aza-compounds, where the link is  $\text{:N}\cdot$  instead of  $\text{:CR}\cdot$ , form metal-complexes with salts of copper, zinc, nickel, cobalt, chromium, or cadmium which can be made either in substance or on the fibre. The quaternary ammonium salts of the tetra-aryldipyrroazamethines may also be used as wool dyes and converted into the metal salts on the fibre.<sup>117b</sup> Again, the 5-nitroso-2 : 4-diarylpyrroles may be condensed with compounds having a reactive methyl or methylene group, such as 1-*p*-sulphophenyl-3-methyl-5-pyrazolone, giving a brown-violet acid wool dye, or 1 : 3 : 3-trimethyl-2-methylenedihydroindole, giving a base the salts of which dye tanned cotton blue; many examples of this type are quoted.<sup>117c</sup> Similarly, the 5-formyl-2 : 4-diarylpyrroles may be treated with active methyl- or methylene-containing substances such as *N*-methyloxindole, quinaldine methiodide, or 1 : 2 : 3 : 3-tetramethyldihydroindole hydriodide, yielding bases giving salts which dye in varied colours, chiefly bluish-reds on tanned cotton.<sup>117d</sup> Again, 2 : 4-diarylpyrroles with the 5-position free, but which may have a substituent aryl, alkyl, or acylamino-group at 3, condensed with nitroso-compounds such as 4-nitroso-1-aryl-5-pyrazolones, 3-nitrosoindoles, or *p*-nitrosodialkylaminobenzenes,<sup>117e</sup> or with aldehydes derived from heterocyclic ring compounds containing

<sup>117</sup> B.P. 562,754-761 (*a* to *h* in text); B., 1944, II, 308-10.

<sup>118</sup> *Ann. Repts.*, 1945, 30, 83.



nitrogen (1 : 3 : 3-trimethyl-2-formylmethylenedihydroindole and the like), giving orange to red dyes for wool.<sup>117</sup> The reactant can also be a *p*-dialkylaminodiphenyl ketone (such as 4 : 4'-dimethylaminobenzophenone), giving bases yielding salts that are wool blues,<sup>117a</sup> or homocyclic aldehydes<sup>117a</sup> (benzaldehyde, *p*-dimethylaminobenzaldehyde, etc.). Certain azo-dyes have also been prepared (see Azo-Dyes, ref. 32).

### MISCELLANEOUS DYES.

General Aniline & Film Corporation<sup>119</sup> confer solvent solubility on organic dyes by forming their salts with amines of the type  $\text{CHR}'\text{R}''\cdot\text{NHR}$ , where R is hydrogen or alkyl, R, R' are alkyl or *cyclo*alkyl, and in all three R groups not less than eight carbons are involved. Various azo-, anthraquinone, triphenylmethane, and phthalocyanine dyes are so treated; the products are of use for lacquers or synthetic plastics.

The same firm<sup>120</sup> produce special triphenylmethane dyes using arylamines with either straight- or branched-chain alkyl groups of 8—18 carbons, for instance, a green acid dye from  $\alpha$ -naphthaldehyde and phenyldodecylbenzylaminesulphonic acid,  $\text{C}_{12}\text{H}_{25}\cdot\text{NHPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ . L. Chalkley<sup>121</sup> takes triphenylmethane compounds of the type  $p\text{-C}_6\text{H}_4\text{X}\cdot\text{CY}(\text{C}_6\text{H}_4\cdot\text{NAlkyl}_2)_2$ , where X is H or  $\text{NH}_2$ , Y is hydroxyl, alkoxyl, amino, a nitrile, thiol, or sulphonic acid group; these are mercurated with a mercuric salt such as the acetate, giving a mercuri-carbinol, which is converted into a dye by heating with acetic acid and methanol.

E. I. Emerson<sup>121</sup> converts 4-aminoantipyrine or its analogues into indamines or indophenols either by conjoint oxidation with arylamines or phenols or by oxidising 4-arylaminantipyrine, or by conjoint dehydration of nitrosoantipyrine and an arylamine. Three patents on sulphur dyes have been granted to National Aniline and Chemical Co. Brown sulphur dyes are obtained by evaporating to dryness a mixture of 1 : 8-aminonaphtholdisulphonic acid, alkali polysulphide, glucose, and an aldehyde, followed by fusion at 210—330°.<sup>122</sup> In a second case the aldehyde selected is furfuraldehyde.<sup>123</sup> Again, coeramidones and dicoeramidones<sup>124</sup> are sulphurised to give olive and grey dyes; special claim is made to the dark brown dye from 2-*p*-aminophenyl-1' : 2'-benz-3'-azabenzanthrone.<sup>125</sup>

<sup>119</sup> U.S.P. 2,315,870; B., 1945, II, 75.

<sup>120</sup> U.S.P. 2,192,118; B., 1945, II, 266.

<sup>121</sup> U.S.P. 2,325,038; B., 1945, II, 298.

<sup>122</sup> U.S.P. 2,194,201; B., 1945, II, 298.

<sup>123</sup> U.S.P. 2,182,350-1; B., 1945, II, 54.

<sup>124</sup> Cf. B.P. 7398 of 1901; B., 1902, 401.

<sup>125</sup> U.S.P. 2,321,787; B., 1945, II, 209.



# FIBRES, TEXTILES, AND CELLULOSE.

## THE PROTEIN FIBRES.

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It is frequently emphasised that industry derives much that is of first-order importance from the utilisation of research stimulated solely by the curiosity of the investigator, but it is equally true that the cause of pure science and the advancement of our knowledge of fundamental processes of nature owe a great deal to applied scientists, whose activities are, in part, determined for them. This is particularly marked in the field of protein chemistry, where the results of work on the constitution of wool, silk, and artificial fibres are not only of great industrial significance, but also throw light on the constitution and behaviour of proteins in general. Many of the papers which have appeared during the year under review serve to illustrate this aspect of research in applied science.

### THE PROPERTIES AND PRODUCTION OF PROTEIN FIBRES.

*Silk.*—Silk fibroin is an insoluble fibrous protein built from long peptide chains which are linked in one direction by bonds arising from the union of carbonyl groups in one chain with imino-groups in an adjacent chain, and in another direction by hydroxyl-hydroxyl or by ether linkings derived from hydroxyl groups contained in serine residues.<sup>1</sup> Sulphur linkings are absent, and there are few, if any, salt linkings. As would be expected, the protein is soluble in aqueous cupriethylenediamine, but it has been shown<sup>2</sup> that neutralisation of such a protein solution results either in renatured protein or in a mixture of renatured and denatured forms according to the conditions of dissolution. If the renatured fibroin is dialysed, a water-clear solution is produced from which the protein is not immediately precipitated on acidification, but separates as a gel in two or three days; evaporation of a layer of an aqueous solution of renatured fibroin yields a film which can be stretched to three times its original length. Acidification of the mixed form causes precipitation of a denatured protein at pH 3. These phenomena have been explained by postulating that the long chains of normal fibroin are oriented parallel to the fibre axis and are in the fully extended  $\beta$  configuration (as in  $\beta$ -keratin). The amino-acids comprising the chains are not distributed in the simple manner suggested by M. Bergmann and E. Niemann,<sup>3</sup> for although the greater part of the chain shows a regular periodicity, there are in each repeat two regions, relatively small

<sup>1</sup> D. Jordan-Lloyd, *Proc. Roy. Inst. Chem.*, 1945, 220.

<sup>2</sup> D. Coleman and F. O. Howitt, *Nature*, 1945, 155, 78.

<sup>3</sup> *J. Biol. Chem.*, 1938, 122, 577; A., 1938, III, 210.



and placed symmetrically between the chains, that are rich in tyrosine and include all of the four proline residues. On dissolution in cupriethylenediamine, CO·NH linkings between adjacent chains are broken and each cupriethylenediamine residue combines with two imino-groups along the whole length of the chain (the ratio of copper to fibroin-nitrogen is approximately 1 : 2). This is followed by the slower process of the folding of each long chain on itself at the two proline-containing centres (probably at a prolyltyrosylprolyl grouping) to give a three-limbed configuration. Neutralisation of the cupriethylenediamine complex yields the fibroin in a renatured and folded form. Denaturation is therefore an unfolding of molecular chains—a view which was also put forward by W. T. Astbury and R. Lomax<sup>4</sup>—but in the case of silk at least, the folded chain still has the  $\beta$  configuration, for the X-ray photograph of a stretched film of renatured fibroin is identical with that of fibroin powder. It is interesting to note, however, that the denaturation of blood fibrin is accompanied by a change from the  $\alpha$  to the  $\beta$  photograph, and W. T. Astbury,<sup>5</sup> being of the opinion that the phenomena described above differ fundamentally from those connected with true denaturation, makes a distinction between denaturation and the aggregation of proteins which are already in an extended form. Apart from its contribution to the structure of silk and to the general problem of protein denaturation, the paper of Coleman and Howitt<sup>2</sup> provides a method for converting insoluble silk fibroin into a soluble form, so that the more standard methods for determination of molecular weight may now be applied to silk fibroin.

*Wool.*—Investigations on wool are complicated by the presence of sulphur in the fibres, but new methods have been developed to overcome this difficulty, and these should also find application in the study of other proteins. The earliest method<sup>6</sup> of determining the constitution of a protein was to hydrolyse with acid and then isolate the amino-acids liberated. This proved to be difficult, but in recent years the development of new methods,<sup>7</sup> including isotopic dilution<sup>8</sup> and microbiological techniques,<sup>9</sup> and the partition chromatographic method of A. J. P. Martin<sup>10</sup> and his collaborators, have yielded more reliable data. The most recent values for the amounts (in g.) of the various amino-acids obtained from 100 g. of dry wool are as follows<sup>11</sup>: alanine 4.1,

<sup>4</sup> *J.C.S.*, 1935, 846; *A.*, 1935, 922.

<sup>5</sup> *Nature*, 1945, 155, 501.

<sup>6</sup> E. Abderhalden *et al.*, *Z. physiol. Chem.*, 1907, 52, 348, and other papers in this journal.

<sup>7</sup> A. C. Chibnall, *J. Soc. Leather Trades' Chem.*, 1946, 30, 1; *A.*, 1946, III, 448; *C.*, 1946, 121. A. J. P. Martin and R. L. M. Synge, "Advances in Protein Chemistry," 1945, p. 2.

<sup>8</sup> D. Rittenberg and G. L. Foster, *J. Biol. Chem.*, 1940, 133, 737; *A.*, 1940, II, 264. S. Graff, D. Rittenberg, and G. L. Foster, *ibid.*, 745; *A.*, 1940, III, 590.

<sup>9</sup> E. F. Gale, *Biochem. J.*, 1945, 39, 46; *A.*, 1945, II, 304.

<sup>10</sup> R. Consden, A. H. Gordon, and A. J. P. Martin, *ibid.*, 1944, 38, 224; *C.*, 1945, 193.

<sup>11</sup> J. B. Speakman, *J. Soc. Arts*, 1945, 93, 603; *B.*, 1946, I, 8.



arginine 8.6, aspartic acid 7.27, amide-nitrogen 1.18, cystine 11.8, glutamic acid 16.0, glycine 6.5, histidine 0.7, hydroxylysine 0.1, leucine 9.7, lysine 2.5, methionine 0.35, phenylalanine 1.6, proline 7.2, serine 9.5, threonine 6.6, tryptophan 0.7, tyrosine 6.1, valine 5.5. Since this method of approach is slow, work has proceeded simultaneously on the properties of the fibre as a whole. Measurement of the resistance of fibres to attack and study of the mechanism of their reactions have been particularly successful. Wool is surprisingly susceptible to change; *e.g.*, when it is ground in a steel ball mill, the cystine content falls markedly, although the carbon and nitrogen contents are unaffected, and aqueous extracts contain increasing amounts of nitrogen, cystine, sulphate, and partly oxidised sulphur compounds as the time of grinding increases.<sup>12</sup>

When wool fibres are heated at 55° in presence of mercury and water vapour, they are stained black by deposition of mercury sulphide.<sup>13</sup> The sulphide is distributed throughout the fibre, but deposits are often localised in certain regions. This observation has been made the basis of a method devised by K. M. Rudall<sup>14</sup> for studying the distribution of sulphur in hair cells. The section of hair to be examined is treated for 48 hours in 0.2M-mercuric chloride in 0.1N-hydrochloric acid, washed in water, and then placed in a sealed tube in contact with water vapour and heated at 78° for 24 hours. It is shown that neighbouring keratin cells may have widely different sulphur contents, and changes in the form of sulphur on cornification of the protein are demonstrated.

Attack by other compounds which remove sulphur has been utilised in another way. After heating human hair for one week in 25% aqueous ammonia, E. Lehmann<sup>15</sup> noticed only very slight change, although the liquor contains yellow sulphides and decomposition products of melamine colours present in the hair. Prolonged treatment results in hydrolysis and breakdown of the structure into fusiform cells which are considered to be the ultimate structural units. The cells have a tendency to burst; they fibrillate readily and are bound together in the fibres by an amorphous substance. After ten months of reaction, the fibre is very much greater in diameter, but still gives an X-ray diagram similar to that of  $\alpha$ -keratin. Fusiform cells are also isolated<sup>16</sup> by digesting wool for 24 hours in 1% aqueous Leonil, washing in hot water, and digesting in 0.5% filtered aqueous Pancreatin-PS of pH 8.6 for 5 hours at 40°. After washing, the residue is gently rubbed with water in an unglazed porcelain mortar and the resulting milky liquid contains the cells in suspension. Treatment of wool with a 30% solution of formaldehyde for 2—3 hours at 150° makes it possible to separate the epidermal membrane from the main stem of the fibre. The epidermis has a true membrane structure and is

<sup>12</sup> B. Edwards and J. I. Routh, *J. Biol. Chem.*, 1944, **154**, 593; A., 1945, II, 32.

<sup>13</sup> J. B. Speakman, C. A. Cooper, and E. Stott, *J. Text. Inst.*, 1936, **27**, T183, T186, T191; B., 1936, 1033.

<sup>14</sup> *Proc. Leeds Phil. Soc., Sci. Sect.*, 1944, **4**, 178; A., 1946, III, 521.

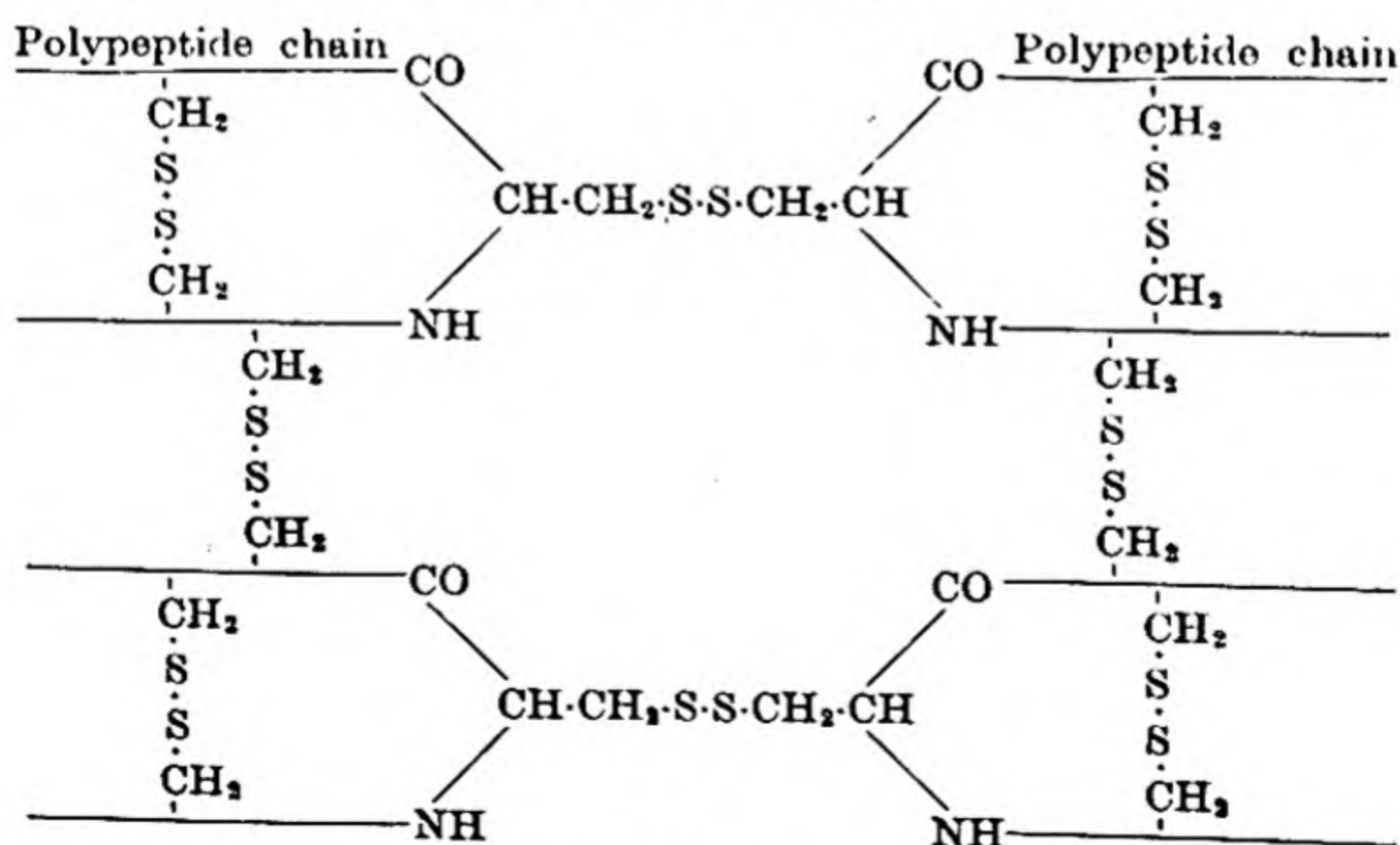
<sup>15</sup> *Textil' er.*, 1943, **24**, 1; B., 1945, II, 134.

<sup>16</sup> E. Elöd and H. Zahn, *ibid.*, 245; B., 1944, II, 351.



considered by E. Lehmann<sup>17</sup> to be similar to the bast of plant stems, and to play a protective rôle in animal fibres.

Sulphur is largely present in wool as the disulphide linkings, but work by H. Phillips and his colleagues<sup>18</sup> points to the conclusion that cystine-sulphur may be divided into various fractions of differing reactivity. When wool reacts with sodium bisulphite, only 50% of the cystine is converted into cysteine and *S*-cysteinesulphonate. The reactive half (fraction *A* + *B*) and the unreactive half (fraction *C* + *D*) may each be divided further into two sub-fractions; *A* which yields water-labile cysteine and *S*-cysteinesulphonate side-chains, and *B* in which these side-chains are stable to water, *C* which is inert, and *D* which decomposes, particularly at temperatures above room temperature, to give combined  $\alpha$ -aminoacrylic acid. A similar fractionation based on differing reactivity with weak alkalis is also possible.<sup>19</sup> One half of the total cystine-sulphur decomposes to yield sulphur and combined lanthionine (the presence of this group of atoms in wool after treatment with ammonia, sodium carbonate, sodium sulphide, or caustic soda has been demonstrated by A. Schöberl<sup>20</sup>), while the other yields combined  $\alpha$ -aminoacrylic acid, hydrogen sulphide, and sulphur. It has been found<sup>21</sup> that the portion of the cystine-sulphur which yields lanthionine is identical with fraction *A* + *B*, and fraction *C* + *D* is responsible for the production of combined  $\alpha$ -aminoacrylic acid when wool is treated with alkalis. Sub-fraction *A* yields lanthionine more rapidly and at lower alkalinities than does *B*, and *D* is converted into combined  $\alpha$ -aminoacrylic acid by alkalis and sodium bisulphite more readily than is sub-fraction *C*. Fraction *C* + *D* may not, therefore, be linked between the peptide chains as is *A* + *B*, and it has been suggested that the sulphur of the two fractions is incorporated in the wool molecule as follows :



<sup>17</sup> E. Elöd and H. Zahn, *Textilber.*, 1944, 25, 1; B., 1945, II, 11.

<sup>18</sup> *Biochem. J.*, 1942, 36, 428; B., 1942, II, 426.

<sup>19</sup> W. R. Cuthbertson and H. Phillips, *ibid.*, 1945, 39, 7; B., 1945, II, 210.

<sup>20</sup> *Ber.*, 1943, 76, [B], 970; A., 1946, II, 125.

<sup>21</sup> H. Lindley and H. Phillips, *Biochem. J.*, 1945, 39, 17; B., 1945, II, 210.



When wool is treated with potassium cyanide all the cystine-sulphur is converted into combined lanthionine.

The fibrous form of wool protein has resulted in the development of specialised techniques such as the study of load-extension curves and the measurement of set and of supercontraction. The results obtained by such methods must, however, be interpreted with discrimination, largely on account of the lack of information on the fundamental properties of fibres. In this connexion, the results recorded in a paper by H. B. Bull<sup>22</sup> indicate that the stress in human hair is due mainly to internal energy and only slightly to entropy changes. It is interesting to note that the modulus of elasticity of fibres has been determined by measuring the velocity of sound in them.<sup>23</sup> Elastic properties are modified by the presence of water or water vapour. According to A. B. D. Cassie,<sup>24</sup> some water molecules are adsorbed on to active centres while others are in a mobile form, and interchange of molecules in the two groups may take place to give a free energy of interchange or mixing. Distribution between the two forms is determined by the condition that the total free energy of the phase should be a minimum. In order that the wool-water isotherm may be analysed satisfactorily<sup>25</sup> it is necessary to reduce the existing isotherms to those for water absorbed under constant hydrostatic pressure, for the vapour pressure observed for water absorbed in a structure such as the wool fibre is influenced by the mechanical restraint. Since this is connected with the amount of swelling, the water vapour pressure also depends on the swelling. Suitable correction may be made for this, and the isotherms so deduced are striking on account of their non-sigmoid character. This leads Cassie to the view that the sigmoid character of most isotherms is due simply to the mechanical properties of the fibres. Moreover, the adsorption hysteresis of wool is shown to be largely due to mechanical hysteresis of the fibres. Analysis of the reduced water isotherm gives a value of 1.12 mols. of localised energy sites per 100 g. of wool, and since there are 1.12 mols. of carbonyl groups per 100 g. of wool, it is suggested that they are the primary water-attracting groups. The figure of 3500 cal. per mol. is given for the heat of adsorption on to the sites. Water adsorbed at regains less than 10—12% largely occupies localised sites in wool, and at greater regains the water is increasingly non-localised. In the opinion of H. B. Bull,<sup>26</sup> protein molecules in the solid state are linked together to form coherent planes, the exposed surfaces of which are hydrophilic; water is adsorbed between these planes. The theory of Cassie has also been applied to a study of the permeability of keratin films to water vapour.<sup>27</sup> If a film

<sup>22</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 533; *B.*, 1945, **II**, 300.

<sup>23</sup> J. W. Ballou and S. Silverman, *Text. Res.*, 1944, **14**, 282.

<sup>24</sup> *Trans. Faraday Soc.*, 1945, **41**, 450; *A.*, 1946, **I**, 19.

<sup>25</sup> *Idem*, *ibid.*, 458; *A.*, 1946, **I**, 19.

<sup>26</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1499; *A.*, 1945, **I**, 24.

<sup>27</sup> G. King, *Nature*, 1944, **154**, 575; *Trans. Faraday Soc.*, 1945, **41**, 479; *A.*, 1946, **I**, 17.



of horn is set up to separate an evacuated space from one containing water vapour, diffusion is slow until the film attains a water content of about 6%, and then there is a rapid increase in the passage of water in spite of decreased pressure across the membrane. Measurements of the rate of diffusion at various pressure gradients and temperatures reveal that the diffusion coefficient is a function of the water concentration and the temperature, but is independent of the elasticity of the keratin lattice. Since the rate of adsorption of water vapour by wool is almost entirely governed by the heat evolved and consequent rise in temperature of the fibres during adsorption, a direct study of the diffusion of water into fibres is impossible. Information on the diffusion process has, however, been obtained<sup>28</sup> by measuring the adsorption of alcohols by wool and horn, in which cases the heating effects are considerably reduced. The adsorption isotherm for wool and ethyl alcohol is similar to that for wool and water, but the sigmoid character is not so pronounced. Molecular adsorption is much smaller—0.45 mol. of ethyl alcohol at saturated vapour pressure as compared with 1.5 for water. The results are satisfactorily interpreted in terms of the diffusion coefficient, which increases with concentration, and show that during the adsorption process a steep front is built up which advances through the medium as adsorption proceeds.

*Protein Rayons.*—As viewed by W. T. Astbury,<sup>5</sup> the fundamental operation in the production of synthetic protein fibres is the unfolding of suitable corpuscular protein molecules (casein, seed globulins, and soya bean) by the action of denaturing agents (alkalis, concentrated solutions of urea, detergents), and drawing out of the liberated chains into elongated configurations. These yield an X-ray photograph of the oriented  $\beta$  type, which according to the experiments of F. R. Senti, M. J. Copley, and G. C. Nutting<sup>29</sup> is not produced by any after-treatment of extruded fibres unless water is present. Proteins obtained from ground-nuts include the globulins, arachin and conarachin, and are extracted by treatment with 0.1—0.2% aqueous caustic soda solution.<sup>30</sup> In the manufacture of Ardil,<sup>31</sup> the solution is filtered and the protein precipitated by addition of sufficient acid or sulphur dioxide to bring the pH of the solution to pH 5; after settling, it is washed free from salts and dried. The first method<sup>32</sup> of producing fibres by denaturation with a 35% solution of urea was not economical. In a more satisfactory method, a 20—30% solution of the protein in dilute alkali is prepared, the pH of the liquor being not less than 12.5,<sup>33</sup> and since the viscosity

<sup>28</sup> G. King, *Nature*, 1944, **154**, 575; *Trans. Faraday Soc.*, 1945, **41**, 325; A., 1945, **I**, 244.

<sup>29</sup> *J. Physical Chem.*, 1945, **49**, 192.

<sup>30</sup> D. Traill and A. McLean, *J.S.C.I.*, 1945, **64**, 221; B., 1945, **III**, 131.

<sup>31</sup> D. Traill, *Chem. and Ind.*, 1945, 58; B., 1945, **II**, 134; *Ind. Chem.*, 1945, **21**, 71; B., 1945, **II**, 105.

<sup>32</sup> A. C. Chibnall, K. Bailey, and W. T. Astbury, B.P. 467,704; B., 1938, 47.

<sup>33</sup> Imperial Chem. Industries, B.P. 537,740; B., 1941, **II**, 343.



of these solutions varies with pH, temperature, and the previous history of the protein, these factors must be controlled. In practice, the solution is matured until its viscosity is between 50 and 300 poises, when it is spun into a coagulating bath containing 15% of sodium sulphate and 1% of sulphuric acid, the temperature being maintained between 25° and 40°. The filaments are partly hardened with a solution of formaldehyde and may then be treated with sulphur dioxide,<sup>34</sup> to improve their resistance to degradation by hot liquids. Reactive compounds containing chlorine,<sup>35</sup> and anhydrides or ketens,<sup>36</sup> are also effective for this purpose, as is a saturated solution of sodium chloride to which is added a small amount of formaldehyde and hydrochloric acid (less than 2%).<sup>37</sup> The fibres have a soft, wool-like handle, and are crimped. Their tensile strength is 10 kg. per sq. mm., elongation at break 50–100%, heat of wetting 19 g.-cal. per g., and their water adsorption similar to that of wool.

Casein fibres are produced similarly and laboratory experiments on the properties of fibres formed by extrusion of casein solutions into coagulating baths containing sodium sulphate, sulphuric acid, and aluminium salts, followed by hardening in acidic formaldehyde liquors, reveal that variation of the viscosity of the casein solution between 67 and 299 poises has no significant effect on the tensile strength of the fibres.<sup>38</sup> The fibres spun from solution containing 20% of casein at pH 10.4 are not so strong as those spun at pH 9.2 or 6.7. Stretching after precipitation increases strength, and stretching in presence of hardening agents causes still further increase. The strongest fibres have a dry strength of 1.0 g. per denier, a wet strength of 0.5 g. per denier, and an elongation at break of 52%. New methods of producing casein fibres include extruding a fine dispersion of casein at a pH greater than 4.6 at 50–70° into a bath containing acetic acid, acetic anhydride, formaldehyde, glycerol, and ethyl alcohol.<sup>39</sup> A fibre of increased strength is prepared by spinning a 1% solution of casein containing sodium lauryl sulphate and lime into a bath containing phosphoric acid and an alkaline-earth phosphate, while casein threads hardened in a liquid of pH 6–8 and then treated with an aqueous emulsion containing formaldehyde, calcium chloride, and hydrochloric acid have increased resistance to attack by hot liquids.<sup>41</sup> Casein monofil suitable for brush making is made<sup>42</sup> by mixing commercial acid-precipitated casein with 70% of

<sup>34</sup> Imperial Chem. Industries, B.P. 492,677; B., 1939, 254.

<sup>35</sup> *Idem*, B.P. 492,895; B., 1939, 254.

<sup>36</sup> *Idem*, B.P. 495,332; B., 1939, 366.

<sup>37</sup> *Idem*, B.P. 513,910; B., 1940, 30.

<sup>38</sup> R. F. Peterson, T. P. Caldwell, N. J. Hipp, R. Hellbach, and R. W. Jackson, *Ind. Eng. Chem.*, 1945, 37, 492; B., 1945, II, 300.

<sup>39</sup> E. C. Whittier and S. P. Gould, U.S.P. 2,187,534; B., 1945, II, 78.

<sup>40</sup> *Idem*, U.S.P. 2,169,690; B., 1944, II, 353.

<sup>41</sup> Courtaulds, Ltd., B.P. 567,904; B., 1945, II, 213.

<sup>42</sup> T. L. McMeekin, T. S. Reid, R. C. Warner, and R. W. Jackson, *Ind. Eng. Chem.*, 1945, 37, 685; B., 1945, II, 299.



water; after an hour the mixture is forced through holes of 0.3—0.6 mm. diameter, passed through a solution of pH 4.7 containing 2% of formaldehyde, 0.1% of sodium naphthalenesulphonate, and 10% of sodium sulphate, and collected on a reel. Skeins of the filaments are stretched 100% in saturated benzoquinone solution and kept stretched for 24 hours. They may be hardened further under tension with 2% aqueous formaldehyde at pH 4.7. The skeins are washed and cut into lengths, which should be set into brushes by means of a synthetic resin or a rubber which may be vulcanised at a low temperature.

Fibres may be prepared<sup>43</sup> from soya-bean protein by treating the protein hydrolysate with carbon disulphide in caustic soda, oxidising in air, and spinning into a bath containing sulphuric acid and sodium sulphate, the fibres being treated with nitrous acid, washed, and hardened in formaldehyde solution. Soya-bean protein<sup>44</sup> fibres produced by the Ford Motor Co. have an average diameter of 23  $\mu$ ., breaking loads of 11.45 lb. per sq. in. (dry) and 4.24 lb. (wet), 16.1% desorption and 12.9% adsorption regains at 65% R.H. and 70° F., and they swell 18.7% in water and 35.1% in 0.1N-caustic soda solution. Technical improvements applicable to the production of all protein rayons include a preliminary hardening with formaldehyde and ammonia or hexamethylenetetramine, either as a separate treatment or by addition of the reagents to the coagulating bath.<sup>45</sup> If hardening liquids have a density greater than that of the fibres, the tow of freshly formed fibres may be fed continuously onto the surface of the liquid, whereupon it takes up a spiral form in the liquid, and when the necessary amount of hardening has taken place, is withdrawn at a rate equal to that of feeding so that the whole operation may be continuous.<sup>46</sup> An aqueous solution containing formaldehyde and 350—750 g. of sulphuric acid per litre is also an effective hardening agent which improves the resistance of fibres to degradation.<sup>47</sup> Wet stretching of hardened fibres in hot water or in steam, followed by washing in water, drying at temperatures not less than 80°, release from tension, and immersion in water, imparts a crimp to the fibres,<sup>48</sup> while treatment with a lubricating agent such as Lissapol L or Dispersol A prior to insolubilisation is also claimed to be advantageous.<sup>49</sup> Satisfactory fibres are produced<sup>50</sup> from a mixture of solutions of viscose and proteins and a dispersing agent, the coagulating liquor containing 9—10% of sulphuric acid and 23—30% of sulphites. The fibres are stretched by not less than 25% and reeled at 70 m. per min.

In view of the importance of formaldehyde in the preparation of protein

<sup>43</sup> Glidden Co., U.S.P. 2,298,127; B., 1944, II, 355.

<sup>44</sup> W. von Bergen, *Rayon Text. Month.*, 1944, 25, 225; B., 1946, II, 42.

<sup>45</sup> Courtaulds, Ltd., B.P. 570,205; B., 1945, II, 302.

<sup>46</sup> *Idem*, B.P. 565,011; B., 1945, II, 23.

<sup>47</sup> *Idem*, B.P. 564,591; B., 1945, II, 16.

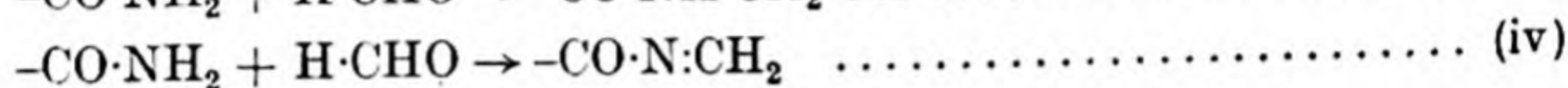
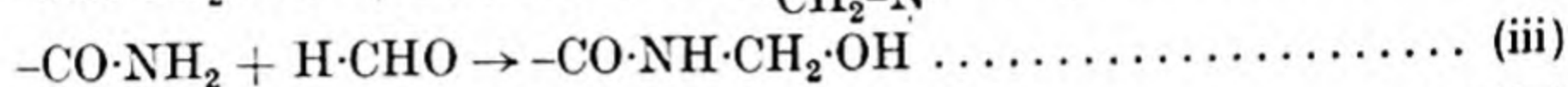
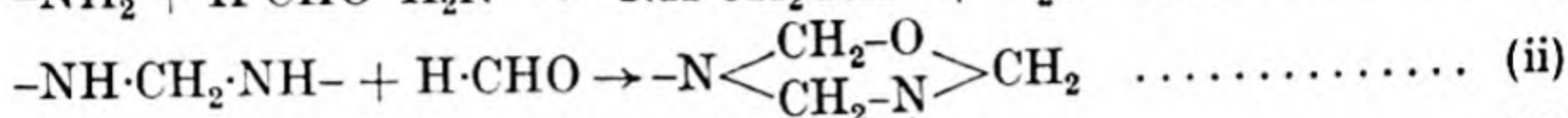
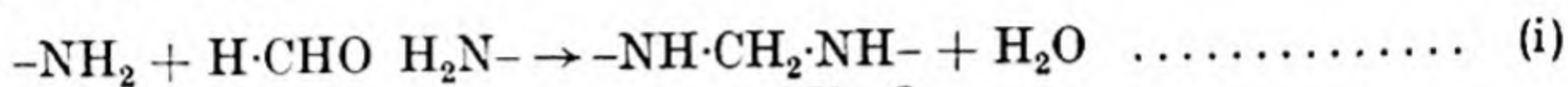
<sup>48</sup> Imperial Chem. Industries, B.P. 570,631; B., 1945, II, 302.

<sup>49</sup> *Idem*, B.P. 570,686; B., 1945, II, 302.

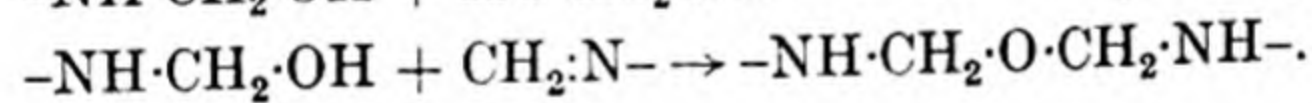
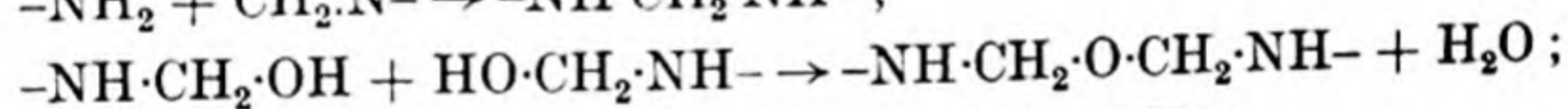
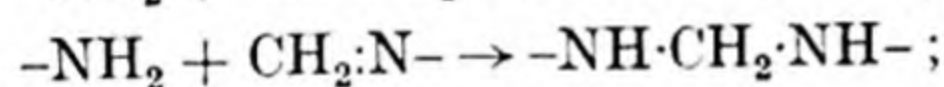
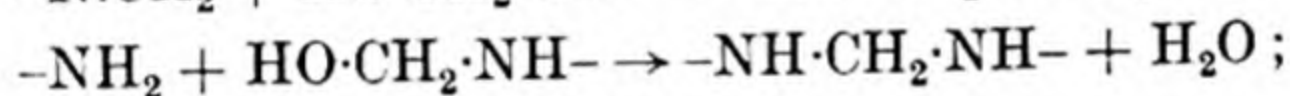
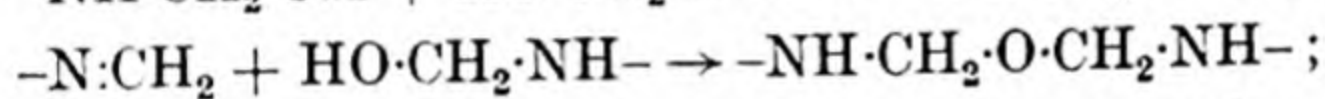
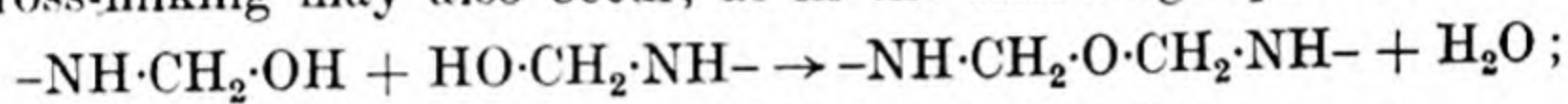
<sup>50</sup> Amer. Enka Corp., U.S.P. 2,318,544; B., 1945, II, 135.



rayons, a paper by R. L. Wormell and M. A. G. Kaye<sup>51</sup> is of considerable interest. It is generally recognised that the  $\epsilon$ -amino-groups of lysine are involved in the reaction with formaldehyde, but from their experimental results, these authors suggest other possibilities. Union might occur between terminal amino-groups of degraded proteins of comparatively low molecular weight with consequent increase in the effective chain length of the protein. Neutral formaldehyde may combine in the manner shown in equations (i) and (ii), while in acid solutions containing salts, where the conditions do not favour ring formation, one amide residue combines with one molecule of formaldehyde as shown in equations (iii) and (iv).



Cross-linking may also occur, as in the following equations.



*Nylons*.—Although, as Miss Jordan-Lloyd<sup>52</sup> has pointed out, the term polyamide as applied to nylon is a misnomer (polyimide is correct as the linking  $\text{CO}\cdot\text{NH}$  is a substituted imido-group), it is still used in technical and patent literature. New methods of manufacturing nylons aim at the production of fibres of improved and widely differing properties, and in a few years' time nylons suitable for any particular purpose should be available. One type is formed<sup>53</sup> by heating equimolecular amounts of a primary diamine and a carboxylic acid, the chain in one reagent being split by an oxygen atom or by an  $\text{SO}_2$  group; *e.g.*, the salt of hexamethylenediamine and  $(\text{CO}_2\text{H}\cdot[\text{CH}_2]_3)_2\text{SO}_2$  is heated in a sealed vessel for 1.5 hours at  $215\text{--}220^\circ$ , and the lower polymer thus formed is heated further for 5 hours at  $200^\circ$  and 0.5 mm. pressure to yield a polyamide of m.p.  $249\text{--}251^\circ$  and intrinsic viscosity of 0.68 poise. When an equimolecular mixture of hexamethylenediamine and adipic acid and an equimolecular mixture of a diamine and a dicarboxylic acid in each or either of which the chain is interrupted by one or more oxygen

<sup>51</sup> *J.S.C.I.*, 1945, **64**, 75; *A.*, 1945, **II**, 264.

<sup>52</sup> *Nature*, 1944, **154**, 486.

<sup>53</sup> *E. I. Du Pont de Nemours & Co.*, U.S.P. 2,191,556; *B.*, 1945, **II**, 268.



atoms, *e.g.*,  $(\text{CH}_2\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{NH}_2)_2$  or  $\text{O}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , are heated together to polymerisation temperature, the fibres formed from the melt have more level-dyeing properties than some other types.<sup>54</sup> Filaments which may be cold-drawn are also produced<sup>55</sup> by heating two polyamides derived from a diamine and a dicarboxylic acid, and an acyclic mono-aminomonocarboxylic acid, *e.g.*,  $\mu$ -aminostearic acid, and by heating<sup>56</sup> a mixture of a long-chain alkylolamine, a glycol and/or a diamine, and a dibasic acid. Fibres of improved softness and pliability are formed<sup>57</sup> from a secondary amino-polyamide (*e.g.*, poly-*NN'*-dimethylhexamethylene adipamide and sebacamide). If nylon filaments which have not been cold-drawn are treated with an aqueous solution of pH not greater than 3 and containing formaldehyde and a catalyst, and baked at 100–150°, they may then not be cold-drawn by more than 75% of their original length.<sup>58</sup> It has also been found<sup>59</sup> that a mixture of a polyamide of high melting point with one of low melting point has a melting point above the average of those of the components.

### THE TECHNOLOGY OF PROTEIN FIBRES.

The growing popularity of synthetic fibres and the recognition of the potentiality of mixture fabrics are helping to break down the old rigid divisions of the textile industry. Indeed, Lord Barnby<sup>60</sup> has expressed the opinion that the manipulation of wool, cotton, flax, silk, and rayon should not now be considered as separate major industries which are largely competitive, but as a single textile industry. In view of this noticeable trend, it is to the advantage of modern textile technologists to be acquainted with advances in the technology of all types of fibres.

*Scouring.*—Unless scouring of both raw wool and of pieces is carried out efficiently, satisfactory results cannot be obtained in any of the subsequent operations. Removal of wool grease from raw wool or of applied oils (usually neutral oils or fatty acids, although a new oiling composition consists<sup>61</sup> of a chlorinated paraffin hydrocarbon, a fatty material such as wool fat, and kerosene) from piece goods must be effected with minimum modification of desirable properties of the fibres. Solvent extraction is the ideal method, for this allows maximum recovery of the extracted oils, and simplifies the preparation of wool fat by-products,<sup>62</sup> but aqueous solutions of soap and alkalis are usually employed on account of their lower cost. The Derby continuous dry-cleaning unit has, however, recently<sup>63</sup> been used for cleaning fabrics from the loom, trichloroethylene being the solvent. It is claimed that certain solvent-scoured fabrics

<sup>54</sup> E. I. Du Pont de Nemours & Co., B.P. 565,350; B., 1945, II, 56.

<sup>55</sup> *Idem*, U.S.P. 2,312,966; B., 1944, II, 315.

<sup>56</sup> *Idem*, U.S.P. 2,312,879; B., 1944, II, 314.

<sup>57</sup> *Idem*, B.P. 568,977; B., 1945, II, 304.

<sup>58</sup> Imperial Chem. Industries, B.P. 565,066; B., 1945, II, 16.

<sup>59</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,193,529; B., 1945, II, 268.

<sup>60</sup> *Hosiery Tr. J.*, 1945, 52, No. 622, 22.

<sup>61</sup> Imperial Chem. Industries, B.P. 569,701; B., 1945, II, 268.

<sup>62</sup> E. S. Lower, *Ind. Chem.*, 1944, 20, 319; B., 1944, II, 360.

<sup>63</sup> Riggs and Lombard, Ltd., *Text. World*, 1944, 94, No. 10, 94.



may be milled successfully with water alone. If solvent-scouring of pieces were the rule, fewer white and yarn-dyed pieces would require crabbing, for this operation is carried out to give the cloths a permanent set so that they are not distorted when treated with scouring liquors at 50° or with dye solutions at the boil. In the manufacture of fabrics such as moquettes it is often necessary to set yarn. This is first twisted into a tight helix and then made into hanks which are boiled in water for some three hours, cooled, and dried. It is clearly important to obtain a maximum setting effect with minimum loss of strength. The optimum pH for setting single fibres has been defined as pH 9.2,<sup>64</sup> but alkaline solutions degrade wool, and it is not advisable to exceed pH 7. In practice, therefore, pH 6.7 is most satisfactory<sup>65</sup> and the time of treatment should not be longer than 3.5 hours. Setting in superheated steam appears to be more efficient than setting in aqueous solutions, but might be difficult to control in practice, as it is imperative that each hank of twisted yarn should receive the same treatment to prevent barriness in the finished cloth.

Removal of size, which in the finishing of wool goods is of minor importance, becomes a major problem in the case of nylon fabrics, and sizes must be chosen which are effective but are easily scoured out. Special plant is available for sizing nylon,<sup>66</sup> and suitable sizes include mixtures of casein, emulsified oils such as castor oil, and an amide, to which gelatin or a sulphated fatty alcohol may be added,<sup>67</sup> an aqueous dispersion of a wool wax, an oil, and casein,<sup>68</sup> gelatin-urea or urea-wax mixtures,<sup>69</sup> or linseed oil,<sup>69</sup> or 4% of polyvinyl acetate.<sup>69</sup> Yarns of more than ten turns per inch are twist set before weaving or knitting by steam setting for 1.5—3 hours, and it is desirable to set nylon fabrics at a temperature not less than 20° above that at which they are to be scoured or dyed—a fact to remember when choosing a size, for this should not be modified so that it becomes difficult to remove.<sup>69</sup> Substances added to reduce static electricity must also be removed in scouring; a typical reagent is an aqueous solution or emulsion containing 2—10% of a lubricating oil and 2—10% of a condensate of ethylene oxide with a higher fatty alcohol.<sup>70</sup> A scouring treatment recommended for nylon is the use of a 1—2% soap solution containing 1.5% (on the weight of the cloth) of sodium phosphate and 1—2% of a synthetic detergent, with a 20—40 : 1 water/cloth ratio.<sup>69</sup>

*Milling and the Production of Unshrinkable Wool Fabrics.*—Although there is no complete agreement<sup>71</sup> regarding the precise mechanism by

<sup>64</sup> J. B. Speakman, *J. Soc. Dyers and Col.*, 1936, 52, 335; B., 1936, 1033.

<sup>65</sup> J. R. Hind and J. B. Speakman, *J. Text. Inst.*, 1945, 36, T19; B., 1945, II, 175.

<sup>66</sup> J. C. E. Bessieres, B.P. 565,570; B., 1945, II, 58.

<sup>67</sup> J. C. E. Bessieres and H. W. Best-Gordon, B.P. 564,027; B., 1944, II, 358.

<sup>68</sup> Lister & Co., B.P. 564,737; B., 1945, II, 22.

<sup>69</sup> G. Loasby, *J. Soc. Dyers and Col.*, 1945, 61, 64; B., 1945, II, 140.

<sup>70</sup> Brit. Nylon Spinners, Ltd., B.P. 563,725; B., 1944, II, 318.

<sup>71</sup> S. A. Shorter, *J. Soc. Dyers and Col.*, 1945, 61, 172; B., 1945, II, 299. A. J. P. Martin, *ibid.*, 173; B., 1945, II, 299. J. Schofield, *ibid.*, 77; B., 1945, II, 135.



which wool fabrics shrink during milling, it is generally recognised that both frictional and elastic properties of the fibres are of importance. The frictional properties of wool fibres have been studied by various methods; J. B. Speakman and his colleagues<sup>72</sup> have used an inclined-plane technique; L. Bchm<sup>73</sup> has measured the force required to pull a uniform sheet of fibres over a glass surface; M. Lipson<sup>74</sup> has measured the force necessary to cause a fibre to move over a cylinder of horn by adding weights to the end of the fibre, while E. H. Mercer<sup>75</sup> has used a modified Bowden and Leben<sup>76</sup> apparatus. All workers have demonstrated that frictional properties of wool fibres differ according to the direction of movement, the value of the coefficient of friction being greater when the scales oppose motion of the fibre. This difference is termed by A. J. P. Martin<sup>77</sup> the "directional frictional effect" (D.F.E.). It arises in part from the scale structure of the fibres, but since it is shown by finger nails and polished porcupine quills, and since wools which have been made non-felting and have no D.F.E. still possess a scale structure, Martin has suggested that it may also arise from a peculiar surface chemical composition. Further support for this view is provided by recent results of M. Lipson<sup>74</sup> showing that the D.F.E. of wool fibres against horn is reduced to one quarter of its original value by treating the horn with reagents which render wool non-felting. The importance of D.F.E. has been stressed by L. Bchm,<sup>73</sup> who has found that the values for the D.F.E. between wool and glass of six different types of wool are in the same order as the milling properties, and that close relationship exists between curves representing the effect of pH on D.F.E. and on milling-shrinkage. Moreover, treatment with sulphuryl chloride, 50% of Solway Green, benzoquinone, or mercuric acetate, which reduces the ability of wool to felt, also reduces the D.F.E. J. Menkart and J. B. Speakman<sup>78</sup> on the contrary have shown that the three last-named treatments cause an increase in the D.F.E. measured against wool fabric using the tilting-plane technique, or against rubber on the lepidometer. They suggest that a modification of fibre scales might result in a reduction of the D.F.E. against glass, even though they show an increase in the D.F.E. against a more flexible surface. Modification of scaliness is certainly responsible for the effectiveness of abrasives<sup>79</sup> in reducing the milling-shrinkage of wool materials. The fabric is impregnated with oil and finely-divided powder (200-mesh silica is the most successful), and mechanically worked. It has been shown by E. H. Mercer<sup>75</sup> that chlorine

<sup>72</sup> J. B. Speakman and E. Stott, *J. Text. Inst.*, 1931, 22, T339; B., 1931, 836.

<sup>73</sup> *J. Soc. Dyers and Col.*, 1945, 61, 278; B., 1946, II, 41.

<sup>74</sup> *Nature*, 1945, 156, 268; *J. Soc. Dyers and Col.*, 1946, 62, 29; B., 1946, II, 123.

<sup>75</sup> *Nature*, 1945, 155, 573; B., 1945, II, 369. *J. Counc. Sci. Ind. Res. Australia*, 1945, 18, 188; B., 1946, II, 41.

<sup>76</sup> *Proc. Roy. Soc.*, 1939, A, 169, 371; B., 1939, 561.

<sup>77</sup> *J. Soc. Dyers and Col.*, 1944, 60, 325; B., 1945, II, 76.

<sup>78</sup> *Nature*, 1945, 156, 143; B., 1946, II, 241.

<sup>79</sup> J. B. Speakman and E. Whewell, *J. Text. Inst.*, 1945, 36, T48; B., 1945, II, 179.



also reduces the differential friction, both coefficients of friction (wool on horn) being reduced by wet chlorination. This author expresses his results rather differently from other workers, making use of a quantity termed the coefficient of frictional difference which he defines as  $\delta = (\mu_2 - \mu_1)/(\mu_2 + \mu_1)$ , where  $\mu_1$  and  $\mu_2$  are the values of the coefficient of friction for motion towards the fibre tip (with the scales) and towards the root (anti-scale). Scaliness is reduced<sup>11</sup> by virtue of the attack of chlorine on the sulphur in wool in accordance with the following primary reaction:  $R \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot R + Cl_2 \rightarrow 2R \cdot CH_2 \cdot SCl$ . When the fabric is subsequently dechlorinated in sodium bisulphite and washed in alkali, each fibre is coated with a layer of degraded protein which swells in washing or milling media, and masks or loosens the scales, thereby preventing fibre travel. This view is supported by the observation that the effectiveness of a standard chlorination treatment is very much reduced<sup>80</sup> on wool treated for several hours with cold dilute caustic soda solution to convert some of the disulphide linkings into  $\cdot CH_2 \cdot S \cdot CH_2 \cdot$  and  $\cdot CH:N \cdot$  linkings. The preliminary alkali treatment also reduces the effectiveness of the sulphuryl chloride and caustic soda processes. It appears that these methods differ fundamentally from wet chlorination, for both reduce the coefficient of directional friction by increasing the lower coefficient of friction.

In contrast to chlorine and bromine, iodine,<sup>81</sup> at least when applied from solution in potassium iodide, does not render wool fabrics unshrinkable. It is taken up (0.2—16%) in three forms, adsorbed, combined and anionic iodine. The combined iodine is probably linked in the form of 3 : 5-di-iodotyrosine groups, but the anionic and absorbed iodine are present as complex polyiodides of the basic side-chains  $R \cdot NH_3 \cdot I_3$ . Technical applications of the halogens to produce non-shrink effects are mainly confined to treatment with gaseous chlorine, or treatment with a solution of sodium hypochlorite, followed by sulphiting. Addition of wetting agents,<sup>82</sup> use of high liquor : cloth ratios, and addition of the hypochlorite in small amounts all help to improve the uniformity of the results. New procedures involve chlorinating at pH 4 and treating with alkaline hydrogen peroxide,<sup>82</sup> or first oxidising with 1—2% potassium permanganate at pH 5—10 and then treating with a dilute solution or suspension of a hypochlorite or nitrogen-chlorine compound.<sup>84</sup>

The protein degradation which accompanies most of the above reactions is not so marked a feature of the group of processes in which polymers are deposited in wool, thereby causing unshrinkability by modifying the elastic properties of the fibres. Ethylene sulphide was one of the first

<sup>80</sup> W. J. P. Neish and J. B. Speakman, *Nature*, 1945, **155**, 45.

<sup>81</sup> S. Blackburn and H. Phillips, *J. Soc. Dyers and Col.*, 1945, **61**, 100; *B.*, 1945, **II**, 217.

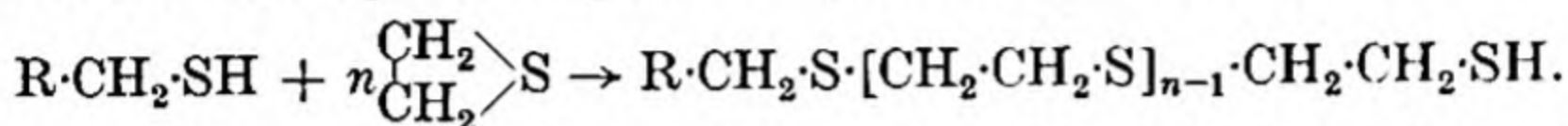
<sup>82</sup> E. B. J. Smith, *Text. J. Australia*, 1943, **18**, 356; 1944, **18**, 425.

<sup>83</sup> Greenwood Dyeing Co., B.P. 564,958; *B.*, 1945, **II**, 21.

<sup>84</sup> Stevensons (Dyers), Ltd., B.P. 569,730; *B.*, 1945, **II**, 272.



to be used in this connexion,<sup>85</sup> the procedure being to expose wool to vapours of ethylene sulphide and water at 50°. Polymerisation takes place inside the fibre and the resulting non-shrink effect is attributed to increased resistance of the fibres to extension. The precise mechanism of the polymerisation is considered by S. Blackburn and H. Phillips<sup>86</sup> to involve first a fission of disulphide linkings by the monothioethylene glycol produced by the action of water on ethylene sulphide. The cysteine side-chains thus produced then condense with one or more molecules of ethylene sulphide to yield long chains thus :



Reactive groups in wool certainly unite with anhydrocarboxyglycine,<sup>87</sup> which polymerises in presence of water and renders wool fabrics unshrinkable. Wool is heated for 6 hours at 50° with 5% of the reagent dissolved in ethyl acetate to which 2% by volume of water is added, and the resulting unshrinkability is due to masking of the surface scales by the film of polymer which is attached to the fibre through basic side-chains, for deaminated wool fabrics are not made unshrinkable by the process. The effect is permanent to treatment with hot organic solvents and the resistance of the treated material to abrasion is three times that of the untreated. Polymerisable inorganic compounds may also be used<sup>88</sup> to produce unshrinkable fabrics by synthesis of the polymer on the surface of the fibres. For example, when a pattern of wool flannel is immersed in a solution of silicon tetrachloride in carbon tetrachloride, vigorous reaction between water in the wool and the silicon chloride yields a siliceous deposit on the surface of the fibres. Deposits of preformed polymers also reduce the shrinking power, but such films are often fairly easily removed. Immersion of wool cloth in a solution of nylon in a strong acid, and then in water to precipitate the nylon, greatly reduces its shrinkage on washing.<sup>89</sup>

*Dyeing.*—The mechanisms of dyeing wool, silk, casein fibre, and nylon have much in common. At high concentrations of dye, the adsorption results may be expressed by the Langmuir adsorption isotherm, but they deviate at low concentrations. B. G. Skinner and T. Vickerstaff<sup>90</sup> interpret this as indicating a more complex mechanism of dyeing than simple salt formation. Amino-groups are important in the dyeing of all four fibres, and in the case of wool, if it is assumed that each amino-group is able to combine with one dye molecule, and not one dye equivalent, the amount of a typical colloidal dye absorbed does not exceed that

<sup>85</sup> T. Barr and J. B. Speakman, *J. Soc. Dyers and Col.*, 1944, **60**, 238; B., 1944, II, 357.

<sup>86</sup> *Ibid.*, 1945, **61**, 203; B., 1945, II, 343.

<sup>87</sup> Imperial Chem. Industries, B.P. 567,501; B., 1945, II, 180. A. W. Baldwin, T. Barr, and J. B. Speakman, *J. Soc. Dyers and Col.*, 1946, **62**, 4; B., 1946, II, 122.

<sup>88</sup> W. J. P. Neish and J. B. Speakman, *Nature*, 1945, **156**, 176; B., 1946, II, 241.

<sup>89</sup> Tootal Broadhurst Lee Co., Ltd., B.P. 567,043; B., 1945, II, 141.

<sup>90</sup> *J. Soc. Dyers and Col.*, 1945, **61**, 193; B., 1945, II, 343.



calculated in terms of the number of amino-groups in the fibres. The saturation value of wool for Solway Blue B at pH 1.6 is fairly close to the maximum acid-combining capacity. Values obtained at pH values less than about 1.5 are higher, but this is probably due to hydrolysis by the acid with production of amino-groups. Similar high values are obtained when the dyeing is carried out in presence of hydrochloric acid. Saturation values for Solway Blue B on silk also correspond with the acid-combining capacity. Although the amount of dye taken up by casein is similar to that taken up by wool, the two fibres have quite different dyeing properties, which are attributed to their different physical structure. It is interesting that when large amounts of dye are applied to wool, it is severely tendered, due to the formation of large dye crystallites inside the water-swollen fibre, and the failure of the dry fibre to accommodate them. The attachment of acid dyes to nylon is not explained solely in terms of amino-groups.<sup>91</sup> At pH values greater than 3, the dyes are linked to end amino-groups, but at lower pH values, there is union with weakly basic NH groups. Acetylation reduces the dye affinity but, as in the case of other fibres, not to the extent expected from the reduced affinity for hydrochloric acid. Dye anions appear to have greater affinity for nylon than for wool, and hence dyeings on nylon are often faster than corresponding dyeings on wool. Nylon is dyed also with direct cotton dyes; the rate of absorption by the fibre is increased<sup>92</sup> by the presence in the bath of less than 1% of a cationic paraffin-chain salt, although addition of 5% of the reagent prevents dyeing. This is attributed to an increase in the degree of aggregation of the dye particles or to adsorption of the reagent followed by the formation of an insoluble dye anion-salt complex. As the concentration of the salt increases, any excess over that required to react completely with the nylon causes the dye to flocculate, and there is probably an exchange between the positively charged nylon and the cations of an insoluble dye-salt complex. With greater amounts of reagent, the insoluble precipitate yields a colloidal solution in the excess of reagent, which merely stains the nylon as both are positively charged. Treatment with acids (sulphuric acid of *d* 1.21—1.23; hydrochloric acid of *d* 1.07—1.075) also increases the affinity of nylon for dyes such as Chlorazol Sky Blue FFS.<sup>93</sup> As would be expected by analogy with other fibres, increased affinity for direct cotton dyes applied from acid baths is imparted to nylon by pretreatment with an aqueous solution containing formaldehyde and cyanamide or one of its derivatives, and heating to produce an insoluble product on the fibre.<sup>94</sup>

Levelness is one of the essential requirements in any commercial dyeing, but is difficult to obtain when a fabric contains tippy wool or has been

<sup>91</sup> R. H. Peters, *ibid.*, 95; B., 1945, II, 216.

<sup>92</sup> J. H. MacGregor and C. Pugh, *ibid.*, 122; B., 1945, II, 216.

<sup>93</sup> Tootal Broadhurst Lee Co., Ltd., B.P. 568,092; B., 1945, II, 180.

<sup>94</sup> Courtaulds, Ltd., B.P. 570,602; B., 1945, II, 343.



unevenly treated with reagents used in carbonising, chlorination, or bleaching.<sup>95</sup> The dye affinity of wool fabrics is affected by exposure<sup>96</sup> to sunlight for two summer months; the take-up of equalising acid colours is reduced, as would be anticipated from a 13% fall in acid-combining capacity. The increase in dyeing capacity which occurs from a sulphuric acid bath is apparent only, as the dye is not fast to washing. Neolan dyes have good fastness to washing on exposed wool. Raw wool blends often contain components of varying dyeing properties, *e.g.*, mixtures of virgin wool, skin wool, and tippy wool, and the following procedure is recommended.<sup>97</sup> The material is wetted out with 0.1% sodium alkyl-naphthalenesulphonate at 135° F. for 10 minutes and after cooling to 80° F., 4% of a protective agent, *e.g.*, a protein degradation product, is added, followed after 10 minutes by the dyes and Glauber salt; ten minutes later 3—5% of acetic acid (56%) is added and after running for 10 minutes the steam is turned on, and the dye liquor is raised to the boil in 45 minutes and boiled for 40 minutes. Formic acid (1—2%) is then added and the liquor boiled for a further 15 minutes; finally dichromate is added and the liquor boiled for a further 50 minutes, after which the wool is rinsed. To rectify unevenness in acid content of carbonised pieces, which might cause unlevel dyeing, thorough washing in almost boiling water is advocated.<sup>95</sup> The difference in dye affinity of treated and untreated wool can, however, be turned to advantage,<sup>98</sup> and good two-tone effects may be obtained by the use of chlorinated and unchlorinated wools. The chlorination must, of course, be uniform and reproducible, and the dyes used should preferably have a low affinity for normal wool, *e.g.*, Solochrome Red ERS. Addition of retarding agents may be useful. It is especially important to control the pH of the dyebath, and the rate at which the temperature of the liquor is raised—automatic regulators have been devised for this purpose<sup>99</sup>—and to keep the time of boiling at a minimum. Differential dye effects may also be produced<sup>100</sup> by impregnating a fabric with a solution of a dye of low affinity and then treating under conditions such that the rate of evaporation of liquid differs in various parts of the material. Similarly, a fabric may be impregnated with resin-forming compounds which affect dye affinity, and localised evaporation afterwards promoted. When the compounds are subsequently polymerised and the fabric is dyed, differential dyeing effects are observed.

Continuous dyeing operations are always theoretically attractive, but mixtures of dyes must be carefully selected so that the components are

<sup>95</sup> T. C. Hutchins, *Amer. Dyestuff Rep.*, 1943, 32, 571.

<sup>96</sup> H. Roesti, *Textilber.*, 1943, 24, 316; B., 1945, II, 109.

<sup>97</sup> J. O'Day, *Amer. Dyestuff Rep.*, 1945, 34, 157.

<sup>98</sup> F. Townend, *J. Soc. Dyers and Col.*, 1945, 61, 144; B., 1945, II, 242; *Text. Rec.*, 1944, 61, No. 741, 48.

<sup>99</sup> Taylor Instrument Companies of Canada, Ltd., *Canad. Text. J.*, 1944, 61, No. 25, 47.

<sup>100</sup> Courtaulds, Ltd., B.P. 564,131; B., 1944, II, 357.



absorbed at similar rates.<sup>101</sup> Loose wool may be dyed<sup>102</sup> continuously with indigo using two sets of four scouring bowls, connected by carrying aprons. The wool is moved through the trough by rakes and squeezed after each immersion, being fed into the first bowl of the machine at 550 lb. per hour from a hopper. It is wetted out in the first bowl, impregnated with vatted indigo in the second (4% of indigo is introduced and the vat contains 3—4 g. of indigo per l., caustic soda, sodium hydro-sulphite, ammonia, and glue), oxidised with hydrogen peroxide in the third bowl, and rinsed in the fourth. It is then passed through a fifth bowl containing indigo so that a further 3.5% of dye is applied, and through an oxidising bath and two bowls containing water for rinsing. The material passes through the machine in 45 minutes, each dip in the indigo occupying 6 minutes.

Finally, mention should be made of a unique method<sup>103</sup> of staining fibres, which although of no practical significance is of primary importance biologically, and might conceivably be developed into a more elegant method of hair dyeing than by use of oxidative dyes. When white rats are injected with 20—30 mg. of 9-phenyl-5 : 6-benzoisalloxazine certain areas of the coat (the growing parts) are coloured orange-yellow due to deposition of the dye or a simple derivative. Although the action of the above reagent is not specific, its manifestation is much greater than those of compounds in which the phenyl group is replaced by methyl, ethyl, propyl, or butyl radicals.

*Miscellaneous Finishing Processes and Testing.*—Limitation of space does not permit discussion of the advances in finishing operations such as moth-proofing,<sup>104</sup> waterproofing,<sup>105</sup> rot-proofing,<sup>106</sup> carbonising,<sup>107</sup> and raising.<sup>108</sup> Interesting developments in the testing of raw materials and finished cloths are shown in the measurement of moisture content<sup>109</sup> of, and small amounts of damage in, textile materials,<sup>110</sup> tensile strength,<sup>111</sup>

<sup>101</sup> H. E. Millson, *Amer. Dyestuff Rep.*, 1945, **34**, 284.

<sup>102</sup> W. von Bergen, T. Crowley, and W. Brommelsiek, *ibid.*, 53.

<sup>103</sup> A. Haddow, L. A. Elson, E. M. F. Roe, K. M. Rudall, and G. M. Timmis, *Nature*, 1945, **155**, 379.

<sup>104</sup> T. F. Webb and G. A. Campbell, *Chem. and Ind.*, 1945, 156. Hizone Products Ltd., U.S.P. 2,340,328. M. H. Hoepli, U.S.P. 2,351,359. H. von Philipp, U.S.P. 2,350,814. J. R. Geigy A.-G., U.S.P. 2,343,071. Sec. of Agric., U.S.A., U.S.P. 2,318,201; B., 1945, II, 141.

<sup>105</sup> A. B. D. Cassie and S. Baxter, *Nature*, 1945, **155**, 21. *Idem*, *Trans. Faraday Soc.*, 1944, **40**, 546; A., 1945, I, 93. E. I. Du Pont de Nemours & Co., U.S.P. 2,313,742; B., 1945, II, 22.

<sup>106</sup> A. C. Neish, G. A. Ledingham, and A. G. Mackey, *Canad. J. Res.*, 1945, **23**, F, 198; B., 1945, II, 305.

<sup>107</sup> G. Nitschke, *Textilber.*, 1942, **23**, 548; B., 1944, II, 316.

<sup>108</sup> Courtaulds, Ltd., B.P. 570,696—7; B., 1945, II, 305.

<sup>109</sup> Heberlein & Co., A.-G., B.P. 569,439; C., 1945, 289. N. W. Gillam, *Text. J. Australia*, 1943, **18**, 324, 358, 394; 1944, **18**, 427, 466. W. R. Lang, *Pastoral Rev.*, 1944, **54**, 393.

<sup>110</sup> C. S. Whewell and H. J. Woods, *J. Soc. Dyers and Col.*, 1944, **60**, 148; C., 1945, 24.

<sup>111</sup> Staff of the Testing Department, Shirley Institute, B.C.I.R.A., *J. Text. Inst.*, 1945, **36**, s1. A. W. Bayes, *ibid.*, 1944, **35**, s41.



resistance to wear,<sup>112</sup> shrinkage,<sup>113</sup> thermal properties,<sup>114</sup> resistance to bacterial attack,<sup>115</sup> and waterproof<sup>116</sup> characteristics of fabrics, levelness of yarns,<sup>117</sup> and fineness,<sup>118</sup> uniformity,<sup>119</sup> and vegetable matter<sup>120</sup> and grease<sup>121</sup> contents of raw wool. A recently published<sup>122</sup> specification for the testing of narrow fabrics contains many useful tests which are applicable to most types of cloth.

<sup>112</sup> Taber Instrument Corp., *Rayon Text. Month.*, 1945, 26, 197. H. F. Schiefer, H. T. Stevens, P. B. Mack, and P. M. Boyland, *J. Res. Nat. Bur. Stand.*, 1944, 32, 261; B., 1945, II, 54.

<sup>113</sup> S. W. Frazier, *Text World*, 1944, 94, No. 12, 136. J. E. P. Furness, B.P. 571,795; C., 1946, 21. N. H. Chamberlain and J. Menkart, *J. Soc. Dyers and Col.*, 1945, 61, 286; C., 1946, 21.

<sup>114</sup> C. W. Hock, A. M. Sookne, and M. Harris, *J. Res. Nat. Bur. Stand.*, 1944, 32, 229; B., 1945, II, 12. S. Baxter and A. D. B. Cassie, *J. Text. Inst.*, 1943, 34, T41.

<sup>115</sup> B. Schulze and H. Sommer, *Textilber.*, 1943, 24, 105; B., 1945, II, 105.

<sup>116</sup> A. B. D. Cassie and S. Baxter, *J. Text. Inst.*, 1945, 36, T67; B., 1946, II, 160.

<sup>117</sup> J. G. Martindale, *J. Text. Inst.*, 1945, 36, T35. N. H. Chamberlain, *J. Soc. Dyers and Col.*, 1945, 61, 161; C., 1945, 290.

<sup>118</sup> H. Doehner, *Züchtungskunde*, 1943, 18, 154.

<sup>119</sup> E. M. Pohle, L. N. Hazel, and H. R. Keller, *U.S. Dept. Agric., Circ.* 704, 1944.

<sup>120</sup> H. J. Wollner, L. Tanner, and I. Michelson, *Amer. Dyestuff Rep.*, 1944, 33, 375. M. Lipson, *ibid.*, 1945, 34, 250.

<sup>121</sup> Amer. Chem. Paint Co., U.S.P. 2,192,614; C., 1945, 170.

<sup>122</sup> *J. Text. Inst.*, 1944, 35, s7; C., 1945, 23.

## CELLULOSE TEXTILE CHEMISTRY.

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### STRUCTURE AND CONSTITUTION OF CELLULOSIC MATERIALS.

THE chemistry of cellulose has now reached a stage at which the correlation of data can give some general idea of the behaviour of cellulose when in textile form. It must be admitted that the gaps in the pattern serve to emphasise the slowness of our progress but the productive lines of research are becoming more clear. A review by W. Badgley, V. J. Frilette, and H. Mark<sup>1</sup> led them to the conclusions that both the size and shape of the molecules and the presence of amorphous areas are closely related to important mechanical properties of cellulose fibres, while polymolecularity is of interest in determining the behaviour of spinning solutions. It was inferred that cellulose molecules, when in solution, assume a moderate undulation; a possible means of determining the accessibility of hydroxyl groups by an exchange reaction with deuterium oxide was also noted. In valuable experimental papers on this subject A. M. Sookne and M. Harris<sup>2</sup> have measured the mechanical

<sup>1</sup> *Ind. Eng. Chem.*, 1945, 37, 227; B., 1945, II, 210.

<sup>2</sup> *J. Res. Nat. Bur. Stand.*, 1943, 30, 1; B., 1944, II, 310. *Ind. Eng. Chem.*, 1945, 37, 478; B., 1945, II, 300.



properties of cellulose acetate films covering a wide range of chain-lengths and chain-length distribution. They find that tensile strength is less sensitive to variations in chain-length than is either elongation or cracking, although the latter remains constant at chain-lengths greater than 150 glucose units. For a given weight-average chain-length the fractions are superior in properties to the blends. A qualitative conclusion, which requires confirmation, is that the mechanical properties of mixtures parallel the weight-averages of their components. In this connexion also N. Gralen and O. Samuelson<sup>3</sup> have found for viscose fibres that a high chain-length and a narrow distribution correspond to high strength and low alkali-solubility.

Much of the knowledge of molecular properties of cellulose has been based on the viscosity of its solutions; the present year shows that an intense interest in flow properties is still maintained despite the development of other tools. W. J. Lyons<sup>4</sup> has pointed out that the various equations relating viscosity of polymer solutions to their concentration neglect the influence of velocity gradient and he suggests that, for cuprammonium solutions of cellulose at least, this may lead to incorrect derivations of the intrinsic viscosity. On this basis the author proposes an empirical modification of the Baker-Philippoff equation which satisfies experimental data for cellulose in cuprammonium solutions. Possible alternatives to cuprammonium as a cellulose solvent for viscosity purposes receive constant study and E. L. Lovell<sup>5</sup> recommends aqueous dibenzyl-dimethylammonium hydroxide (Triton F); intrinsic viscosities of cotton and wood samples in this solvent were found to vary linearly with the intrinsic viscosities of corresponding nitrocelluloses. S. Coppick<sup>6</sup> found, on the other hand, that the use of the nitrate, especially for wood celluloses, is superior to determination of viscosity in either cuprammonium or cupriethylenediamine solution. The same author finds<sup>7</sup> that the relation between concentration and viscosity is a function of heterogeneity and suggests that measurements of intrinsic viscosity are inaccurate unless some heterogeneity coefficient is included. For cellulose acetate solutions this refinement is unnecessary; this has been demonstrated in a paper in which are described the effects of concentration, temperature, solvent, acetic acid yield, and heterogeneity on the viscosities of cellulose acetates.<sup>8</sup> Other points of interest here are that the Baker equation is advocated for the derivation of intrinsic viscosities and that oxidation of secondary cellulose acetate with periodic acid results in an increase in its viscosity in acetone solution. M. Takei<sup>9</sup> has also considered the

<sup>3</sup> *Svensk Papperstidn.*, 1945, 48, 1; *Chem. Abs.*, 1945, 3157.

<sup>4</sup> *J. Chem. Physics*, 1945, 13, 43; *A.*, 1945, I, 142.

<sup>5</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 683; *C.*, 1945, 25.

<sup>6</sup> *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 7; *B.*, 1945, II, 106; *C.*, 1945, 106.

<sup>7</sup> *Ibid.*, 1944, 119, *TAPPI Sect.*, 256; *B.*, 1945, II, 106.

<sup>8</sup> F. Howlett, E. Minshall, and A. R. Urquhart, *J. Text. Inst.*, 1944, 35, T133; *B.*, 1945, II, 134.

<sup>9</sup> *Kolloid-Z.*, 1942, 101, 129; *A.*, 1945, I, 59; cf. *A.*, 1942, I, 364.



viscosity of cellulose acetate in various solvents with particular reference to the Baker equation and to the equation  $1/[\eta'] = ac + 1/k$ , where  $[\eta']$  is the Philippoff-Hess constant. The constants  $a$  and  $k$  are connected with association and solvation in the solution and are shown to be correlated with the well-known function  $\mu^2/6\sigma$ , which is reputed to have characteristic values for solvents, swelling agents, and non-solvents.

Despite the necessity and value of the above type of work it is still essential to find by independent methods the relation between viscosity and molecular weight for each polymer-solvent system. This relation is now usually expressed in the form  $[\eta] = KZ.M^a + b$ , where  $b$  is very small. Staudinger suggested that  $a$  was unity and found  $KZ$  by osmotic pressure and end-group methods. Recently<sup>10</sup> A. M. Sookne and M. Harris have made a study of this problem using cellulose acetate fractions of a higher degree of homogeneity than has hitherto been obtained and calibrating the viscosity method with osmotic pressure measurements. They reach the most important conclusion that, for acetone solutions,  $a = 1$ , although it is clear from their data that small deviations from this figure could not easily have been detected. A rather similar study<sup>11</sup> for fractions of cellulose acetate butyrate gave a value of 0.83 for  $a$ , which is shown also to be valid for the heterogeneous material when degraded in various ways. Means of obtaining viscosity-average and number-average molecular weights from a single determination of viscosity are also given. A paper by R. Simha<sup>12</sup> offers an interpretation of the modified Staudinger rule and relates the exponent  $a$  of the molecular weight to a flexibility parameter  $p$  varying between zero and unity. A relation between the molecular weight and the sedimentation and diffusion constants is also found in terms of  $p$  and the values of the latter determined for cellulose esters and starch derivatives by viscosity, sedimentation, and diffusion methods show satisfactory agreement.

By far the most important work on sedimentation since the publication of Svedberg and Pedersen's book is a long thesis by N. Gralen.<sup>13</sup> It is quite impossible adequately to summarise this paper, which deals with sedimentation, diffusion, and viscosity of celluloses, nitrocelluloses, sodium cellulose xanthate, and sodium cellulose glycollate. Molecular weights, polydispersity, and molecular shapes are determined and it is concluded that the relation between intrinsic viscosity and molecular weight is not linear.

Methods of measuring molecular weight that are new in principle are infrequent. One such for determining weight-average molecular weights is based on earlier theoretical work by Debye.<sup>14</sup> It involves measurement of the turbidity and the change in refractive index with concentration

<sup>10</sup> *Ind. Eng. Chem.*, 1945, 37, 475; B., 1945, II, 300.

<sup>11</sup> J. W. Tamblyn, D. R. Morey, and R. H. Wagner, *ibid.*, 573; A., 1945, I, 272.

<sup>12</sup> *J. Chem. Physics*, 1945, 13, 188; A., 1945, I, 223.

<sup>13</sup> *Thesis, Uppsala*, 1944; A., 1944, I, 153.

<sup>14</sup> P. M. Doty, B. H. Zimm, and H. Mark, *J. Chem. Physics*, 1945, 13, 159; C., 1945, 200; cf. A., 1944, I, 175.



and has been illustrated by reference to cellulose acetate and polystyrene fractions. Comparable osmotic pressure data are also included.

D. R. Morey and J. W. Tamblyn<sup>15</sup> report results of a fractional precipitation of cellulose acetate butyrate in which the amount precipitated was ascertained from light-scattering data and they find good agreement between the distribution curves obtained optically and gravimetrically.

Many of the properties of cellulose acetate depend on its acetic acid content and it is of interest that experimental methods for the acetylation of rayons without a change in chain-length have been published.<sup>16</sup> The methods are based on the early work of Hess with pyridine and acetic anhydride. In this connexion also, P. Popov<sup>17</sup> has shown that replacement of pyridine by dioxan when acetylating with acetyl chloride results in a more efficient reaction, although the author makes no mention of whether changes in chain-length occur during the process.

So far data relating only to individual cellulose molecules have been discussed here. The arrangement of these within the fibre is clearly important and, as might be expected, the use of X-rays for diagnostic purposes is still in vogue. K. Hess<sup>18</sup> for instance has secured X-ray photographs of raw cotton fibres at various stages of growth and by comparison with fibres freed from pectins, fats, waxes, proteins, phosphatides, carbohydrates, and impurities, has been able to give a rough picture of the position of these constituents in the primary cell wall. Using the ultra-violet microscope with swollen fibres the lamella of the secondary wall is shown to exist as thread-like fibrillæ 2000—3000 Å. thick. Another aspect of X-ray work is the assessment of crystalline matter in cellulose and with the additional help of specific birefringence data P. H. Hermans<sup>19</sup> suggests that between 20 and 30% is present in ramie. Some account of fibre patterns of cellulose esters and mixed esters has also been given.<sup>20</sup>

In connexion with the determination of the amount of non-crystalline matter in cellulose Nickerson's method,<sup>21</sup> in which the carbon dioxide evolved in the initial, rapid, stages of hydrolysis with hydrochloric acid—ferric chloride is measured, has been modified by C. C. Conrad and A. G. Scroggie.<sup>22</sup> From observations with glucose it is suggested that before the reaction slows down appreciably one mol. of carbon dioxide per mol. of glucose has been evolved. The amorphous area of native, mercerised, and regenerated celluloses, measured in this way, was found to decrease with increasing crystallinity as calculated from X-ray diffraction data. The reporters stress that variants on this type of method have for long

<sup>15</sup> *J. Appl. Physics*, 1945, **16**, 419; A., 1946, I, 46.

<sup>16</sup> F. Howlett, *J. Text. Inst.*, 1944, **35**, T123; B., 1945, II, 134.

<sup>17</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **46**, 325; A., 1945, II, 226.

<sup>18</sup> *Textilber.*, 1943, **24**, 289; B., 1945, II, 105.

<sup>19</sup> *Rec. trav. chim.*, 1944, **63**, 13; B., 1946, II, 283.

<sup>20</sup> W. O. Baker, *Ind. Eng. Chem.*, 1945, **37**, 246; B., 1945, II, 186.

<sup>21</sup> B., 1941, II, 300.

<sup>22</sup> *Ind. Eng. Chem.*, 1945, **37**, 592; B., 1945, II, 300.



been used and suggest that the greatest caution be exercised before accepting quantitative conclusions although qualitatively the results are doubtless correct.

A reawakening of interest in the densities of fibres is shown by recent papers. Thus from a review<sup>23</sup> of density and X-ray data the conclusion has been drawn that the density of cellulose in water rather than in other media must be regarded as the true density. K. Lauer and U. Westermann<sup>24</sup> have also concluded that the density of cellulose in water is equal to the theoretical crystal density and is unaffected by the presence of non-crystalline material, with the result that measurements in water show no difference for native and cellulose hydrate fibres.

W. Moll<sup>25</sup> advocates the use of suspension methods in the determination of density on account of increased accuracy over pyknometric or gasometric methods. He finds the density of regenerated cellulose to be independent of chain-length, concentration of the viscose solution, or stretching during spinning, but to be influenced considerably by precipitation and drying conditions. A useful review of previous work on this subject (unfortunately appearing in instalments) has been given by J. W. Illingworth.<sup>26</sup>

The adsorption isotherms of purified cotton and viscose rayon for many organic liquids have been studied by K. Lauer,<sup>27</sup> and all deviate from the S-shaped curves characteristic of water, although those for lower alcohols also reflect in some measure the overlapping of adsorption and swelling phenomena. With the exception of acetic acid, which produces swelling only, and of acetone, which is indifferent at low vapour pressures, all other organic liquids produce pure adsorption isotherms with no evidence of swelling. The results are confirmed by measurements of weight- and volume-swelling. The heat of adsorption is found always to be positive, but the differences between cotton and rayon found with water are not present for most organic liquids. On the same general subject is a literature survey of the moisture relations of textiles,<sup>28</sup> while the effects of temperature and humidity on the physical properties of cotton, regenerated cellulose, and nylon tyre-cords have been exhaustively treated by J. H. Dillon and I. B. Prettyman.<sup>29</sup>

An increasing number of papers describe the degradation of cellulose, partly for documentary results or to simulate effects of normal use and industrial processes, but also on account of information required for the fuller understanding of the structure of cellulose. L. J. Heidt, E. K.

<sup>23</sup> P. H. Hermans, J. J. Hermans, D. Vermass, and A. Weidinger, *Rec. trav. chim.*, 1944, 63, 44; A., 1946, I, 204.

<sup>24</sup> *Kolloid-Z.*, 1944, 107, 89; *Chem. Abs.*, 1945, 183.

<sup>25</sup> *Beih. Z. Ver. deut. Chem. A: Chemie, B: Chem. Tech.*, 1943, No. 47, 105; *Chem. Abs.*, 1944, 6091.

<sup>26</sup> *Text. Rec.*, 1944, 62, Aug., 60; Sept., 57, 67.

<sup>27</sup> *Kolloid-Z.*, 1944, 107, 86; *Chem. Abs.*, 1945, 183.

<sup>28</sup> P. W. Carlene, *J. Soc. Dyers and Col.*, 1944, 60, 232; B., 1944, II, 351.

<sup>29</sup> *J. Appl. Physics*, 1945, 16, 159; B., 1945, II, 299.



Gladding, and C. B. Purves,<sup>30</sup> from a review of the literature, conclude that periodates and lead tetra-acetate oxidise glycol in an identical way and assume that any other oxidant producing dialdehyde cleavage in glycols or cellulose must resemble septavalent iodine or quadrivalent lead in its atomic characteristics. From a consideration of extensive physical data it was predicted and confirmed that tervalent silver compounds and perbismuthates should also effect this type of oxidation. In the same paper an explanation based on oxidation potentials is given of the difference in behaviour of sodium chlorite and hypochlorite in the oxidation of cellulose. G. F. Davidson<sup>31</sup> (with T. Brownsett) has continued his study of the oxidation of cellulose with periodic acid by a comparison of the viscosities of nitrated hydrocelluloses and oxycelluloses which were produced by oxidation with dichromates or periodic acid. It was found that where nitrated oxy- and hydro-celluloses from periodic acid had the same viscosity at the same low concentration of solution, then at higher concentrations the derivative from the oxycellulose had the higher viscosity. Such a difference was not present with degraded celluloses produced with dichromates. From these observations it is inferred that during periodate oxidation chemical changes in the cellulose, other than depolymerisation, occur, and this is supported by the fact that under certain conditions the progressive oxidation of cellulose with periodic acid results in a progressive rise in the viscosity of the derived nitrocelluloses. A similar effect during the oxidation of secondary cellulose acetate has also been observed.<sup>8</sup> During the oxidation of dry cotton or rayon with nitrogen tetroxide it has been shown,<sup>32</sup> by liberation of carbon dioxide with concentrated hydrochloric acid, that the number of carboxyl groups formed approaches one per hundred glucose unit. A steady increase in the copper number, however, shows that degradation also occurred although this may have been due to the alkalinity of the solutions used for the measurement of this property. The products of oxidation were found to have a high affinity for basic dyes and the sodium salts dissolved in water to give viscous solutions.

V. C. Ester<sup>33</sup> has studied the degradation of cotton, regenerated cellulose, and acetate rayons by potassium permanganate, sodium perborate, bleaching powder, and chloramine-*T* at different concentrations and temperatures. From determinations of loss in weight, wet strength, copper number, and acetyl content, it was shown that, under mild conditions, acetate rayon is the most resistant but with more drastic treatment cotton cellulose is the best. Several papers on the degradation of cellulose by acids are available for discussion. In the first of these the initial velocity of hydrolysis of cotton, mercerised cotton, and regenerated cellulose by *N*-hydrochloric acid at 35° has been shown<sup>34</sup> to increase in

<sup>30</sup> *Paper Trade J.*, 1945, 121, *TAPPI Sect.*, 81; A., 1945, I, 342.

<sup>31</sup> *J. Text. Inst.*, 1945, 36, T1; B., 1945, II, 135.

<sup>32</sup> K. Maurer and G. Reiff, *J. makromol. Chem.*, 1943, 1, 27; A., 1945, II, 146.

<sup>33</sup> *Iowa State Coll. J. Sci.*, 1944, 19, 15; B., 1945, II, 266.

<sup>34</sup> O. Eisenhut and E. Schwartz, *Chemie*, 1942, 55, 380; B., 1944, II, 352.



the order given, although the total reaction is not one of zero order. Changes in mean chain-length were used as a basis for this conclusion, a procedure which appears to be open to serious errors. Purified wool, silk, nylon, and various natural and rayon cellulose fibres which had been hydrolysed extensively have been examined in the electron microscope.<sup>35</sup> Silk and the natural celluloses were similar in appearance, while the cellulose rayons gave fibrils of greater thickness than those of natural celluloses and the nylons readily gave fibrils which resembled those of degraded wool.

G. Champetier and J. Bonnet<sup>36</sup> find that if cellulose is treated with sulphuric acid of concentration below 770 g. per litre then simple addition occurs, the original cellulose being produced on washing with water. Above this concentration sulphuric acid esters are formed, that at 900 g. per litre corresponding approximately to  $C_6H_9O_5 \cdot SO_3H$ .

R. Beha<sup>37</sup> has described methods for determining  $\alpha$ -cellulose content, copper number, methylene-blue absorption, and alkali-solubility. A direct relation between the first two properties was found and markedly degraded fibres possessed a high alkali-solubility. This last conclusion has been amplified by A. Marschall,<sup>38</sup> who states that when different cellulose samples undergo the same degradation treatment or when the same samples undergo different treatments to the same final mean chain-length, then the different preparations show different solubilities in 10% sodium hydroxide solution.

The effects on the chain-length, strength, and elasticity of regenerated cellulose fibres after bleaching, weathering, repeated washing, and heating in caustic soda solutions have been recorded by H. Rath and W. Meyer.<sup>39</sup> The chain-length was found to be sensitive to small amounts of deterioration, but the mechanical properties changed little unless the fibres were badly damaged. Extensive damage in bleaching was satisfactorily indicated by the decrease in strength produced by boiling the rayon in sodium carbonate solution. It was recommended that both viscosimetric and mechanical tests should be used when considering attack by caustic soda.

R. Meredith<sup>40</sup> has recently published what is probably the most comprehensive record of the tensile elasticity of textile fibres. Detailed data are given for cotton, bast fibres, cellulose rayons, nylon, vinyon, and various protein fibres. Nylon was found to be the most elastic fibre and a comparison of cotton with rayons showed that the order of elasticity for a given stress was cotton, viscose rayon, and acetate rayon, although this order was reversed for a given strain.

The mechanism of the processes used when rayon is treated with

<sup>35</sup> E. Husemann and A. Carnap, *J. makromol. Chem.*, 1943, 1, 16; B., 1945, II, 76.

<sup>36</sup> *Bull. Soc. chim.*, 1943, [v], 10, 585; *Chem. Abs.*, 1944, 4127.

<sup>37</sup> *Ind. textile*, 1941, 58, 335; *Chem. Abs.*, 1944, 2486.

<sup>38</sup> *Zellwolle u Kunstseide*, 1943, 1, 117; *Chem. Abs.*, 1944, 5079.

<sup>39</sup> *Textilber.*, 1943, 24, 353; B., 1945, II, 12.

<sup>40</sup> *J. Text. Inst.*, 1945, 36, T147; B., 1945, II, 369.



acid formaldehyde is considered in some detail by J. Stadler.<sup>41</sup> On drying the rayon the formaldehyde is held loosely as a polyoxymethylene and is then depolymerised under the influence of the catalyst. The amount of the polymer on the fibre increased with increasing concentration of formaldehyde but decreased with rising reaction temperature and increasing catalyst concentration. Prolonged drying caused considerable loss of polyoxymethylene, which is relatively volatile at room temperature, and the conclusion of Götre and Reif, that part of the formaldehyde which is strongly bound to the fibre is in the polymerised form, was not confirmed.

### BAST FIBRES.

The purification of bast fibres for textile purposes has been extensively studied recently. A patented method for flax involves impregnation with acid in the presence of a wetting agent followed by a short treatment with warm sodium chlorite solution, after which non-cellulosic constituents may be removed by boiling in alkali.<sup>42</sup> The use of hot acid sodium chlorite for the removal of lignin is also the basis of an analytical method for the determination of cellulose in jute.<sup>43</sup> The commercial bleaching of jute has been discussed fully by B. P. Ridge and A. H. Little,<sup>44</sup> who state that mild bleaching is achieved with cold alkaline hypochlorite, cold alkaline permanganate, or hot sodium chlorite. Better shades are obtained with an alkaline hypochlorite treatment followed by a hot peroxide bleach. In this most comprehensive paper information is also given on the bleaching of jute in package form or in mixtures with other fibres, and on the woollenising of jute. In a further contribution, these authors, with J. Wharton,<sup>45</sup> describe investigations on the relation of jute incrustants to fibre and yarn strength. Removal of lignin only (with acid chlorite solutions) or of hemicelluloses only (with caustic soda solutions under pressure) results in a low wet strength although the dry strength is little affected. Partial removal of both these incrustants usually reduces both wet and dry strength, although after hot alkaline steeps, such as are given in peroxide bleaching, the dry strength may be increased due to a closer setting of the fibres. Pure, white cellulose suitable for viscose manufacture is obtained by successive treatments with acid hypochlorite, caustic soda under pressure, and alkaline hypochlorite. The browning of bleached jute in sunlight is probably due to residual lignin, since the effect is not apparent when all lignin is removed.

In a chemical means of cottonising hemp the fibres are first heated in caustic soda and then manganese dioxide is deposited in the middle lamella by soaking in potassium permanganate solution. The material is then treated with cold acid hypochlorite, when the manganese dioxide

<sup>41</sup> *Textilber.*, 1942, **23**, 593; B., 1944, II, 317.

<sup>42</sup> G. B. Fowler, B.P. 567,774; B., 1945, II, 213.

<sup>43</sup> P. B. Sarkar and H. Chatterjee, *Sci. and Cult.*, 1944-45, **10**, 340; C., 1945, 106.

<sup>44</sup> *J. Text. Inst.*, 1944, **35**, p121; B., 1945, II, 81.

<sup>45</sup> *Ibid.*, 193; B., 1944, II, 351.



catalyses the localised liberation of chlorine which disintegrates the fibrous structure. Staining tests for bast fibres based on the deposition of gold or of a dyestuff in the middle lamella are also discussed.<sup>46</sup>

### RAYONS.

*Viscose Rayon.*—Three useful papers on the production and properties of viscose rayon have been published. The first is by M. Takei,<sup>47</sup> who, assuming that technical spinning solutions contain the so-called fringed micelles, finds that in the preliminary ripening the particles themselves decrease in size, while their solvation increases. During after-ripening the solvation decreases but the particle size remains unchanged. Effects of alkali and carbon disulphide concentration are also discussed. In the second paper K. Lauer and R. Döderlein<sup>48</sup> show that for viscose rayon manufactured under accurately defined conditions the chain-length, if above 220 glucose units, has no effect on the tensile strength, extensibility, or serviceability. Finally, L. Rose<sup>49</sup> has given a most needed account of the production, physical properties, and dye affinities of Tenasco and Durafil rayons, and in the same paper he reviews the products in which these yarns may be used to the best advantage.

Considering production aspects, a survey of plant sources of cellulose suitable for rayon, together with processes of purification, has been compiled.<sup>50</sup> Changes occurring when sulphite cellulose and raw cotton, impregnated with sodium hydroxide, are stored have been recorded by A. S. Schpitalni<sup>51</sup>; the decrease in cuprammonium viscosity with time was greater for the raw cotton than for the pulp, and the amount of water-soluble acidic compounds in both alkali celluloses increased with time of storage. The preparation of sodium cellulose xanthate by passing soda cellulose and carbon disulphide through a heated zone at temperatures of 45—110° has been claimed, whilst deaëration of viscose can be accomplished by allowing it to flow as a thin film down the wall of a vacuum vessel, the temperature of which is automatically adjusted to produce steam bubbles within the film.<sup>52</sup>

Various patents have been granted for improving the strength, toughness, elasticity, or crimp of viscose yarn by alterations to the spinning process, the most notable being new recipes for the composition of the coagulating bath.<sup>53</sup> For the preparation of protein-containing cellulose

<sup>46</sup> Haller, *Textilber.*, 1943, 24, 6; B., 1945, II, 134; C., 1945, 105.

<sup>47</sup> *Kolloid-Z.*, 1944, 106, 30; A., 1945, I, 59.

<sup>48</sup> *Zellwolle, Kunstseide, Seide*, 1943, 48, 123; *Chem. Abs.*, 1944, 4450.

<sup>49</sup> *J. Soc. Dyers and Col.*, 1945, 61, 113; B., 1945, II, 210.

<sup>50</sup> R. A. Herrero, *Ind. y Quim.*, 1943, 5, 56; B., 1945, II, 239.

<sup>51</sup> *J. Appl. Chem. Russ.*, 1940, 13, 447; B., 1944, II, 310.

<sup>52</sup> Brit. Cellophane, Ltd., B.P. 570,687; B., 1945, II, 302; B.P. 564,153; B., 1945, I, 7.

<sup>53</sup> Amer. Viscose Corp., U.S.P. 2,312,152; B., 1944, II, 354. North Amer. Rayon Corp., U.S.P. 2,315,559–60; B., 1945, II, 137. E. I. Du Pont de Nemours & Co., U.S.P. 2,324,437; B., 1945, II, 240. Courtaulds Ltd., and W. R. Weigham, B.P. 570,159; B., 1945, II, 302.



fibres, viscose can be added to a protein solution to give suspended particles of sizes less than  $10\text{ m}\mu$ . which are stabilised with a dispersing agent, the whole being then spun normally.<sup>54</sup> Rather different modifications of the rayon have been achieved by regeneration in a bath containing either urea and formaldehyde, the yarn being subsequently heated,<sup>55</sup> or a condensation product of a sugar or aliphatic alcohol with ethylene oxide.<sup>56</sup> The impregnation under pressure of rayon staple with a urea-formaldehyde primary condensation product followed by drying and baking is claimed<sup>57</sup> to produce a cardable resilient fibre.

The application of a high-frequency electric field to the rapid drying of rayon cakes has been described in a patent.<sup>58</sup>

*Cuprammonium Rayon.*—A review of the production and properties of cuprammonium rayon has been published by W. L. Ashby.<sup>59</sup> Dyeing, printing, and finishing processes are also adequately dealt with.

When a solution of cellulose in cuprammonium hydroxide is spun into an aqueous alkaline precipitating bath at  $15\text{--}60^\circ$  it is suggested<sup>60</sup> that with copper and ammonium sulphates in the bath the former absorbs ammonia and the latter copper hydroxide. Methods have also been suggested whereby ammonia and copper are washed from fresh cuprammonium yarn in such a way that they can be used again in the spinning processes,<sup>61</sup> while the recovery of ammonia from precipitation liquors can be accomplished by expulsion as an ammonia-steam mixture by direct countercurrent contact with live steam.<sup>62</sup>

*Cellulose Esters and Ethers.*—Four patents have been granted to the Cellulose Research Corporation covering the preparation of wood cellulose suitable for acetylation. Two of these<sup>63</sup> concern the production of pure cellulose from finely-divided wood by means of slight modifications of standard practice; the third<sup>64</sup> starts from unbleached pulp and proceeds by similar methods, while in the fourth<sup>65</sup> an aliphatic acid of low molecular weight and an inert solvent are added to purified wet cellulose; by distillation, the water and solvent are removed together and the fibres are simultaneously activated by the acid. A further way of activating wood pulp for the preparation of high-viscosity esters is to swell in 17% sodium hydroxide solution and, after washing with water, to dry by distillation with ethyl acetate,<sup>66</sup> whilst pretreatment of cellulose with a

<sup>54</sup> Amer. Enka Corp., U.S.P. 2,318,544; B., 1945, II, 138.

<sup>55</sup> L. Ubbelohde, U.S.P. 2,322,981; B., 1945, II, 214.

<sup>56</sup> Amer. Viscose Corp., B.P. 568,394; B., 1945, II, 214.

<sup>57</sup> Röhm & Haas Co., B.P. 569,188; B., 1945, II, 243.

<sup>58</sup> Radio Corp of America, B.P. 563,590; B., 1944, II, 354. U.S.P. 2,325,652; B., 1945, II, 269.

<sup>59</sup> *J. Soc. Dyers and Col.*, 1945, 61, 167; B., 1945, II, 305.

<sup>60</sup> Imperial Rayon Corp., U.S.P. 2,319,428; B., 1945, II, 108.

<sup>61</sup> Amer. Rayon Co., Inc., U.S.P. 2,322,778, 2,322,801; B., 1945, II, 214.

<sup>62</sup> A. Heltmeier, U.S.P. 2,315,201; B., 1944, II, 355.

<sup>63</sup> U.S.P. 2,185,776; B., 1945, II, 16; U.S.P. 2,187,710; B., 1945, II, 78.

<sup>64</sup> U.S.P. 2,180,517; B., 1944, II, 354.

<sup>65</sup> U.S.P. 2,191,525; B., 1945, II, 269.

<sup>66</sup> Brit. Celanese, Ltd., B.P. 563,560; B., 1944, II, 315.



mixture of acetic acid and phosphoric acid is also claimed to be valuable.<sup>67</sup> As a variant on normal procedure the cellulose is pretreated with a mixture of lower aliphatic acids, including formic acid, and a small amount of sulphuric acid, after which the acetic anhydride is added in two stages.<sup>68</sup> Ideas on the ripening of acetylation mixtures appear to be moving towards the use of higher temperatures, and recent patents suggest that this can be accomplished without danger if calcium, magnesium, aluminium, or zinc compounds be added to neutralise the acid catalyst.<sup>69</sup> Addition of similar compounds to the residues in the acetyliser to avoid the cleaning-out process has been advocated.<sup>70</sup>

The acetylation of cellulose in a heterogeneous medium has been studied by Z. A. Rogovin and M. Mironov,<sup>71</sup> by swelling with acetic acid and then adding acetic anhydride, toluene, and perchloric acid; the triacetate is formed in about two hours.

For the preparation of higher esters the Eastman Kodak Co. recommend a pretreatment with either methyl nitrite<sup>72</sup> or a fatty acid<sup>73</sup> before acylating with the corresponding anhydride. In an alternative method an alkyl ester and a complex of boron trifluoride with water or aliphatic acids or esters are used to promote reaction of the anhydride.<sup>74</sup>

Novel methods for the preparation of mixed esters have been suggested. For example, the mixed anhydrides, together with acid catalysts, are used in the presence of a stable chlorofluorobalkane<sup>75</sup>; alternatively an aliphatic acid and the anhydride of another acid may be used together with an aldehyde<sup>76</sup>; acetate formates are produced by direct action of the mixed anhydrides in the presence of one of the corresponding acids and an inorganic acid catalyst.<sup>77</sup> Mixed esters containing dicarboxylic acid groups can be formed by the interaction of a low fatty acid partial ester of cellulose with a dicarboxylic acid or its anhydride such as phthalic anhydride.<sup>78</sup>

In an attempt to lubricate or soften cellulose acetate yarn for subsequent processing Eastman Kodak Co. suggest the use of compounds  $RO \cdot CO \cdot NHR'$  or  $RO \cdot CH_2 \cdot CH(OR') \cdot OR''$ , where R, R', and R'' have the usual all-embracing structures.<sup>79</sup> Up to 25% of some of these can be introduced into the spinning solution or they may be applied to the yarn subsequently. *N*- $\beta$ -Hydroxyethylmorpholine palmitate has a

<sup>67</sup> Eastman Kodak Co., U.S.P. 2,193,033; B., 1945, II, 269.

<sup>68</sup> Brit. Celanese, Ltd., B.P. 565,812; B., 1945, II, 57.

<sup>69</sup> H. Dreyfus, B.P. 566,863; B., 1945, II, 138. Brit. Celanese, Ltd., B.P. 567,893, 568,047, 568,051, 568,098; B., 1945, II, 213; B.P. 568,545; B., 1945, II, 240.

<sup>70</sup> Eastman Kodak Co., U.S.P. 2,318,573; B., 1945, II, 138.

<sup>71</sup> *J. Chem. Ind. (U.S.S.R.)*, 1941, 18, No. 7, 7; *Chem. Abs.*, 1944, 4127.

<sup>72</sup> U.S.P. 2,316,866; B., 1945, II, 79.

<sup>73</sup> U.S.P. 2,315,973; B., 1945, II, 78.

<sup>74</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,316,525; B., 1945, II, 78.

<sup>75</sup> Hercules Powder Co., B.P. 565,179; B., 1945, II, 79.

<sup>76</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,322,575; B., 1945, II, 214.

<sup>77</sup> Brit. Celanese, Ltd., B.P. 568,439; B., 1945, II, 214.

<sup>78</sup> Eastman Kodak Co., U.S.P. 2,183,982; B., 1944, II, 354.

<sup>79</sup> U.S.P. 2,184,008-9; B., 1944, II, 353; U.S.P. 2,186,630; B., 1945, II, 82.



lubricating and an antistatic effect when applied to acetate rayon,<sup>80</sup> while as antistatic agents only a formidable list is given of sulphate, phosphate, or phosphite esters of *cycl*hexanol substituted in the 2-position by hydrocarbon radicals.<sup>81</sup> To reduce electrostatic charge on nylon as well as on acetate rayon an emulsion containing small amounts of a lubricating oil and a condensate of ethylene oxide and a higher fatty alcohol is applied to the threads.<sup>82</sup> Although probably effective for the purposes described, the adverse effect of this type of treatment on machinery seems not to have been considered.

The modification of properties of acetate rayon by additions to the spinning solution is an obvious procedure and several novel effects are claimed by this means. For example, diminished solubility with softening at high temperatures is obtained by including a dialkyl ether of dimethylolurea which is subsequently cross-linked by baking,<sup>83</sup> or by including a compound such as  $X(NH \cdot CO_2R)_2$ , where X is alkylene or arylene and R is aryl or ethenyl alkyl.<sup>84</sup> By incorporating a water-insoluble condensate of formaldehyde and melamine into the spinning solution fibres of subdued lustre are produced.<sup>85</sup> Finally, affinity for direct dyes can be obtained by additions of  $\beta$ -diethylaminoethyl methacrylate or alternatively treating the yarn with a solution of deacetylated chitin.<sup>86</sup> Chemical after-treatments have been applied to increase the extensibility of acetate rayon. In one process<sup>87</sup> the rayon is swollen in a mixture of dichloroethane and methylene chloride. According to X. Soulas<sup>88</sup> this type of treatment leads to brittleness and he advocates spinning a yarn in which only a part can be swollen. As an example, a yarn is wet-spun from a mix of 90% of acetate and 10% of aceto-butyrate, the acetate is saponified by ammonia, and the yarn is then swollen in acetone. The effect of vapours of mineral acids in producing water-sensitive material from acetate rayon has been patented,<sup>89</sup> hydrochloric acid being recommended.

It has been claimed<sup>90</sup> that the degradation of cellulose acetate by ultra-violet light can be inhibited by impregnation with  $\beta$ -naphthyl salicylate.

A useful volumetric method of determining combined sulphate in cellulose esters has been described.<sup>91</sup> Decomposition with a mixture of

<sup>80</sup> Eastman Kodak Co., U.S.P. 2,186,628; B., 1945, II, 82.

<sup>81</sup> *Idem*, U.S.P. 2,318,296; B., 1945, II, 178.

<sup>82</sup> Brit. Nylon Spinners Ltd., G. Loasby, and D. L. C. Jackson, B.P. 563,725; B., 1944, II, 318.

<sup>83</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,317,131; B., 1945, II, 137.

<sup>84</sup> S. Peterson and P. Schlack, U.S.P. 2,320,704; B., 1945, II, 178.

<sup>85</sup> H. C. Olpin and S. A. Gibson, B.P. 565,815; B., 1945, II, 57.

<sup>86</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,191,887; B., 1945, II, 269.

<sup>87</sup> F. B. Hill, B.P. 567,107; B., 1945, II, 141.

<sup>88</sup> *Ind. textile*, 1943, 60, 75; *Chem. Abs.*, 1944, 5668.

<sup>89</sup> J. G. Williams and L. Krause, B.P. 563,133; B., 1944, II, 318.

<sup>90</sup> H. Dreyfus, B.P. 563,287; B., 1944, II, 315.

<sup>91</sup> C. L. Hoffpauir and J. D. Guthrie, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 391; C., 1945, 25.



nitric and perchloric acids is followed by precipitation of barium sulphate with acid barium chromate solution and iodometric determination of liberated chromic acid.

W. A. Dickie<sup>92</sup> has given a brief account of the use of 1-denier Celanese yarns for insulation; also included are methods of dyeing and finishing acetate rayon, and a new process for the production of staple fibre.

Studies of the influence of mercerisation conditions on the ease of subsequent ethylation and benzylation of cellulose and on the properties of the products have shown that a short treatment with 20% sodium hydroxide with addition of potassium chloride during soaking yields products that are easily etherified.<sup>93</sup> Another proposed pretreatment uses first an alkali-stable wetting agent followed by caustic soda of concentration greater than 50%.<sup>94</sup>

Filaments of water-insoluble methylcellulose have been spun from an alkaline solution into urea with the application of up to 100% stretch,<sup>95</sup> whilst extrusion of a low-substituted celluloseglycollic acid has been accomplished from a 6% sodium hydroxide solution at a temperature near to its freezing point.<sup>96</sup>

*Other Rayons.\**—Developments in polyamides for fibres are concerned with alterations in the physical properties by interpolymerisation or by mixing of polymers. For instance, filaments with improved level-dyeing properties can be spun from melts formed by the polymerisation of the usual diamines and dibasic acids with similar compounds in which the hydrocarbon chain is interrupted by oxygen atoms.<sup>97</sup> A further variant in the production of filamentous polyamides is the addition of an acyclic monoaminomonocarboxylic acid such as  $\mu$ -aminostearic acid to the normal amines and acids,<sup>98</sup> while by mixing separately-formed polyamides of different melting points fibres can be drawn having a melting point higher than the average of the components.<sup>99</sup> The stabilising of polyamides to sunlight and water can, it is claimed,<sup>100</sup> be accomplished by spinning in the presence of a small amount of an aryl-oxyacetic acid or its sulphur analogue. Claiming to "modify" polyamide fibres, D. McCreath and Imperial Chemical Industries Ltd.<sup>101</sup> impregnate undrawn filaments with an acid formaldehyde solution and follow this

\* Although not cellulosic in origin these rayons warrant inclusion here on account of their possible future importance. This practice was also followed in the previous Report (1944).

<sup>92</sup> *J. Soc. Dyers and Col.*, 1944, 60, 332; B., 1945, II, 76.

<sup>93</sup> S. N. Uschakov and N. V. Orlova, *J. Appl. Chem. Russ.*, 1944, 17, 193; B., 1945, II, 266.

<sup>94</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,190,450; B., 1945, II, 178.

<sup>95</sup> *Idem*, and W. J. C. Amend, B.P. 569,878; B., 1945, II, 302.

<sup>96</sup> *Idem*, U.S.P. 2,190,445; B., 1945, II, 178.

<sup>97</sup> *Idem*, B.P. 565,350; B., 1945, II, 56.

<sup>98</sup> *Idem*, U.S.P. 2,312,966; B., 1944, II, 315.

<sup>99</sup> *Idem*, U.S.P. 2,193,529; B., 1945, II, 268.

<sup>100</sup> *Idem*, B.P. 568,688; B., 1945, II, 241.

<sup>101</sup> B.P. 565,066; B., 1945, II, 16.



by baking. The properties of nylon tyre-cords have been discussed by G. Loasby<sup>102</sup> with emphasis on the high tensile and impact strength, low inflation growth, and high elastic modulus required for such textiles.

A group of compounds similar to the polyamides can be formed by condensing a mixture of an alkylolamine, a glycol, a diamine, and a dibasic acid; such polymers can be drawn into filaments which show orientation along the fibre axis.<sup>103</sup>

The only improvement noted in ethylene polymers is a method of reducing the heat-shrinkage by heating while under tension followed by treatment at a lower temperature in a relaxed state; in an example quoted the shrinkage temperature is reputed to be raised from 40° to 95°.<sup>104</sup> Details have been given of the wet-spinning of polyvinyl esters containing free hydroxyl groups the products of which can be stretched in steam.<sup>105</sup>

The literature of alginate rayons is growing considerably, and J. B. Speakman and his colleagues have published two papers, in the first of which<sup>106</sup> details for the production of satisfactory yarns are given, while the second paper<sup>107</sup> gives a summary of the properties of some of these yarns and serves to emphasise their restricted usefulness. An 8% solution of sodium alginate is extruded into a bath containing calcium chloride, hydrochloric acid, olive oil, and Lissapol C to give filaments with a minimum denier of two and a strength of about 2 g. per denier. The calcium salt can be converted into the more resistant beryllium or chromium salts; the latter may also be produced by after-treatment of alginic acid threads themselves. The physical characteristics of alginate rayons from some six different metals are described. These rayons are very hygroscopic and isotherms for the absorption and desorption of water vapour are given. The water absorption and strength increase with increasing metal content; the standard yarns have a density of about 1.8 and are completely non-inflammable. Aluminium, chromium, and beryllium alginates are only slightly weakened by alkalis (which dissolve the calcium rayon) but on account of their low extensibility cannot be woven or knitted, and it is recommended that fabrics should first be made as the calcium salt, to be converted in piece form into other metal derivatives. Three patents<sup>108</sup> dealing with the production of calcium alginate threads from the sodium salt and vice versa have been accepted.

<sup>102</sup> *Trans. Inst. Rubber Ind.*, 1945, 20, 140; B., 1945, II, 175; cf. B., 1944, II, 278.

<sup>103</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,312,879; B., 1944, II, 314.

<sup>104</sup> *Idem*, B.P. 564,584; B., 1945, II, 22; U.S.P. 2,325,060; B., 1945, II, 268.

<sup>105</sup> R. P. Roberts, E. B. Johnson, and H. H. Taylor, B.P. 563,960; B., 1944, II, 366.

<sup>106</sup> J. B. Speakman and N. H. Chamberlain, *J. Soc. Dyers and Col.*, 1944, 60, 264; B., 1945, II, 13.

<sup>107</sup> N. H. Chamberlain, A. Johnson, and J. B. Speakman, *ibid.*, 1945, 61, 13; B., 1945, II, 135.

<sup>108</sup> Courtaulds Ltd., and R. B. Hall, B.P. 567,641; B., 1945, II, 213. Courtaulds Ltd., and E. E. Tullis, B.P. 568,177; B., 1945, II, 213. Courtaulds Ltd., H. J. Hegan, and J. H. Givens, B.P. 569,212; B., 1945, II, 241.



For those requiring a general review, the production, properties, and uses of the newer fibres have been described.<sup>109</sup>

### SIZING.

As regards cellulose this section is represented by a single patent<sup>110</sup> for the use of aqueous mixtures of starch and urea with rayons.

The whole of the remaining information concerns polyamide textiles. In a paper on the processing of nylon yarns and fabrics, G. Loasby<sup>111</sup> recommends linseed oil, or mixtures of urea with gelatin or waxes, as sizes and gives details of scouring. Compositions containing casein, castor oil, and urea,<sup>112</sup> or casein, oils, and waxes with antiseptic and antistatic agents,<sup>113</sup> have been claimed, while for knitting of sheer hosiery a plasticised water-insoluble but water-sensitive protein may be used.<sup>114</sup> Patents for the use of mixtures of partly saponified polyvinyl acetate and boric acid have also been granted.<sup>115</sup>

### SCOURING, BLEACHING, AND MERCERISING.

The chemistry of the enzymic splitting of starch has been discussed with special reference to the merits of pancreatic, bacterial, and malt-amylase preparations.<sup>116</sup> None of these affects the chain-length of the cellulose and the rate of disappearance of the iodine-starch colour, which is used as a measure of dextrinisation, decreases in the same order; methods of control and analysis are also described. Desizing before kier-boiling can, it is stated,<sup>117</sup> be effected by passing the cloth through warm  $\frac{1}{2}\%$  sulphuric acid and setting aside for about three hours. A series of tests of the effect of organic solvents emulsified with the kier liquor on the wax content, whiteness, and tensile strength of cotton fabrics has shown that the wax content is least, and the wettability greatest, in the absence of solvent, and that the various solvents used differ little in effectiveness.<sup>118</sup>

A. L. Dubeau and H. R. Dinges<sup>119</sup> describe the wide applications and advantages of sodium bicarbonate in place of acid for the removal of residual caustic from fabrics. According to a recent patent,<sup>120</sup> a means is provided for removing water-insoluble soaps from cloth by rinsing it in a bath containing  $\frac{1}{2}\%$  of sulphamic acid.

<sup>109</sup> Anon., *Chem. Met. Eng.*, 1945, 52, No. 1, 119; B., 1945, II, 134.

<sup>110</sup> Stein, Hall & Co., Inc., U.S.P. 2,192,198; B., 1945, II, 272.

<sup>111</sup> J. Soc. Dyers and Col., 1945, 61, 64; B., 1945, II, 140.

<sup>112</sup> J. C. E. Bessieres and H. W. Best-Gordon, B.P. 564,027; B., 1944, II, 358.

<sup>113</sup> Lister & Co., Ltd., W. Garner, F. G. Holroyd, Allied Colloids (Bradford) Ltd., G. Langley, and R. Gill, B.P. 564,737; B., 1945, II, 22.

<sup>114</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,312,469; B., 1944, II, 319.

<sup>115</sup> *Idem*, U.S.P. 2,317,728; B., 1945, II, 112; U.S.P. 2,324,601; B., 1945, II, 272.

<sup>116</sup> H. Rath, D. Keppler, and I. Roesling, *Textilber.*, 1944, 25, 18, 58; B., 1945, II, 20.

<sup>117</sup> Amer. Cyanamid Co., U.S.P. 2,185,548; B., 1945, II, 21.

<sup>118</sup> M. B. Desai, B. K. Vaida, and K. Venkataraman, *J. Indian Chem. Soc., Ind. Ed.*, 1944, 7, 140; B., 1945, II, 305.

<sup>119</sup> *Amer. Dyestuff Rep.*, 1944, 33, 219; B., 1945, II, 19.

<sup>120</sup> Proctor & Gamble Co., U.S.P. 2,316,379; B., 1945, II, 82.



A combination of bleaching and scouring is attained by using an alkaline solution of a hypochlorite, a chlorite, and a detergent at low temperatures to cause bleaching followed by raising the temperature to complete the scouring.<sup>121</sup>

In two German papers the value of hypochlorite and peroxide methods has been discussed. In the first<sup>122</sup> the following sequence is preferred for the bleaching of cotton or cotton-rayon mixtures: wetting out, cold alkaline hypochlorite, warm alkaline hydrogen peroxide. In the second<sup>123</sup> rather similar conditions for the individual processes are advocated but it is stressed that a combination of a hypochlorite with a peroxide bleach is not suitable for rayons because of the reduction of strength occasioned.

A series of important articles<sup>124</sup> reports the whole process of continuous peroxide bleaching, in which the kier is replaced by a steam J-box; the cloth moves at more than 250 yards per minute through the various steeping and heating units.

Standard methods for the analysis of bleaching powder and bleach liquors have been published in detail.<sup>125</sup>

The sole paper on mercerising is a review of the subject by W. Döhle<sup>126</sup> in which the changes occurring in fibres, as indicated by chemical tests, by X-ray evidence, and by microscopical examination, are discussed, and methods of measuring the degree of mercerisation from dye affinity, from X-ray data, and from chemical reactivity are compared.

### DYEING.

In addition to the more technical literature of patents and articles concerned with dyeing practice there is a considerable number of valuable scientific papers on the fundamental aspects of the subject. These are becoming ever more necessary as a background of summarised knowledge and are described here at the outset.

In a review of the literature on the dyeing of cellulose with direct dyes, H. A. Standing<sup>127</sup> has considered in detail the purification of dyes, equilibrium dyeing, the diffusion of dyes into cellulose, and theories of dyeing and substantivity. In connexion with the structural conditions necessary for substantivity to cotton of azo-dyes, H. H. Hodgson and E. Marsden<sup>128</sup> support the theory that conjugated chains are necessary by an interpretation in terms of resonance and hydrogen bonding. In their view, which they support by examples, the aryl rings must be coplanar for substantivity. In all research on the adsorption of dyes

<sup>121</sup> Mathieson Alkali Works, B.P. 566,291; B., 1945, II, 81.

<sup>122</sup> G. Duschle, W. Kling, and G. Simon, *Textilber.*, 1943, 24, 21; B., 1945, II, 140.

<sup>123</sup> H. Baier and W. Hundt, *ibid.*, 73; B., 1945, II, 108.

<sup>124</sup> D. J. Campbell, *Amer. Dyestuff Rep.*, 1944, 33, 293; B., 1945, II, 215. Buffalo Electro-Chem. Co., Inc., *ibid.*, 345, 365, 385, 405; B., 1945, II, 216.

<sup>125</sup> Anon., *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 141; C., 1945, 160.

<sup>126</sup> *Textilber.*, 1943, 24, 430; B., 1944, II, 316.

<sup>127</sup> *Trans. Faraday Soc.*, 1945, 41, 410; B., 1945, II, 305.

<sup>128</sup> *J. Soc. Dyers and Col.*, 1944, 60, 210; B., 1944, II, 316.



by textiles some quantitative measure of dye uptake is required and a description has been given<sup>129</sup> of the relative merits of standard methods. For dyes in solution chemical means are of limited use and satisfactory colorimetric methods are described. The latter can also be used for dyed fibres either *in situ* or by removing the dye with a solvent, and details for accomplishing this are given. A special photoelectric instrument measures the rate of dyeing by continuously recording the concentration of dye solutions circulated over a sample of fabric. An experimental survey has been made<sup>130</sup> of the absorption of Brenthol dyes by cellulose under different conditions of temperature and dye and salt concentration. Substantivity, which decreased with rise of temperature, varied widely with the dye, being least for Brenthol AS and greatest for Brenthol BN, and with the exception of two dyes the substantivity was in the decreasing order viscose rayon, cuprammonium rayon, cotton, and linen. The Freundlich adsorption equation was found to represent most of the results. H. Schumacher<sup>131</sup> has classified direct dyes according to the temperature of their optimum absorption by cuprammonium and viscose rayons. Data are given in the paper relating the time of dyeing to the amount of dye taken up at the low temperature and it is shown that the time to attain fibre saturation is the same for hot and cold dyeing. The degree of absorption for cold dyeing is in general equal to or less than for hot dyeing, but uniformity of dye penetration is more difficult to attain. The arrangement of dye-stuffs on ramie fibres has been studied with the aid of fluorescing dyes, which were found to be arranged longitudinally on the fibres, the fluorescent light emitted by the dyes being polarised in the same direction.<sup>132</sup> T. Vickerstaff<sup>133</sup> has discussed a means of measuring the brightness of dyes and from data for a large number of dyes of different hues has concluded that those having only one adsorption band edge in the visible spectrum are more efficient than those with two.

Light-fastness values obtained for twenty-two substantive dyes on cotton have shown that colours comprising a range of wave-lengths such as red-brown or red-orange have the best fastness. The relative merits of various artificial light sources are discussed and the Ostwald and the German "Echtheitskommission" fastness scales compared.<sup>134</sup> C. A. Seibert and C. A. Sylvester<sup>135</sup> have demonstrated that vat-dyed, mildly alkaline cotton is markedly inferior in light-fastness to neutral or mildly acid cotton.

<sup>129</sup> E. Waters, *ibid.*, 200; C., 1944, 169.

<sup>130</sup> C. H. Giles, *ibid.*, 280; B., 1945, II, 19.

<sup>131</sup> *Textilber.*, 1943, 24, 231, 268; B., 1944, II, 356.

<sup>132</sup> H. Ziegenspeck, *Kolloid-Z.*, 1944, 106, 62; B., 1945, II, 57.

<sup>133</sup> *Proc. Physical Soc.*, 1945, 57, 15; B., 1945, II, 108.

<sup>134</sup> Research Textielfonds 1931, Enschede, *Textilber.*, 1942, 23, 541; B., 1944, II, 316.

<sup>135</sup> *Amer. Dyestuff Rep.*, 1944, 33, 311; B., 1945, II, 19.



According to S. H. Mhatre and G. M. Nabar<sup>136</sup> the oxidation by sodium hypochlorite of cotton dyed with Caledon Yellow G and Indanthrene Yellow FFRK, which are not altered by the hypochlorite, results in a ratio of aldehyde to carboxyl groups of two. When Indanthrene Blue R or Ciba Blue, which are altered by the hypochlorite, are used, this ratio is unity, which is taken to indicate that a different oxidation reaction occurs. The same authors<sup>137</sup> (with K. S. Bhujang) find that with Ciba Blue on the cotton the rate of decomposition of sodium hypochlorite is initially more rapid than decomposition in blank experiments and that the increased rate depends on the amount of dye present. The subject matter of these papers appears to need further investigation.

Of current interest is a paper in which the chromium and iron contents of commercial khaki-dyed textiles are recorded together with their fastness to light, washing, perspiration acids, and chlorine.<sup>138</sup>

In a discussion on special methods of dyeing with indanthrene colours, F. Gund<sup>139</sup> has described a method whereby the cloth is treated at 85—90° for half an hour with a very fine suspension of the dye, after which caustic soda and sodium hydrosulphite are slowly added. Dyeing is complete after a further half hour and the concentration of alkali determines the final shade and degree of adherence of the pigment. The functions and influences of various (I.G.) auxiliary agents are also considered. Provided that the dye solution is preheated, then the Indanthrene-Anthrasol-Naphtol AS range of dyes may also be dyed at 40—45°. <sup>140</sup> Protection has been obtained<sup>141</sup> for the use of hot solutions of *m*-tolylenediamine and related compounds for the prevention of tendering by sulphur black dyes.

The modification of the dyeing properties of viscose rayon by condensing resins in the fibre is well-known, and a specific case of this has recently been patented.<sup>142</sup> The fibres are soaked in a solution containing formaldehyde and the guanidine salt of an unsaturated carboxylic acid, such as methacrylic acid; after baking they have a soft handle and an improved dye affinity, especially for wool dyes.

The well-known difficulty of producing deep shades on delustred acetate rayons is reputed to be overcome by depositing a condensate of melamine and formaldehyde on the fabric followed by dyeing with dispersed dyes.<sup>143</sup> Of considerable interest in this field is the discovery that when acetate rayon is subjected to pressure, say with embossing rollers, then the compressed areas can be saponified more easily than the

<sup>136</sup> *Current Sci.*, 1944, 13, 256; B., 1945, II, 110.

<sup>137</sup> *Ibid.*, 281; B., 1945, II, 110.

<sup>138</sup> S. R. Ramachandran and V. R. Wadekar, *J. Indian Chem. Soc., Ind. Ed.*, 1944, 7, 71; B., 1945, II, 106.

<sup>139</sup> *Textilber.*, 1943, 24, 435, 470; B., 1944, II, 356.

<sup>140</sup> E. Köster, *ibid.*, 265; B., 1944, II, 356.

<sup>141</sup> Southern Dyestuffs Corp., U.S.P. 2,193,328; B., 1945, II, 305.

<sup>142</sup> Courtaulds Ltd., and J. H. MacGregor, B.P. 568,628; B., 1945, II, 271.

<sup>143</sup> H. C. Olpin and S. A. Gibson, B.P. 568,438; B., 1945, II, 242.



uncompressed areas, and by using suitable dyes a coloured, patterned effect can be produced.<sup>144</sup>

Differential dyeing effects have been obtained on cotton, rayon, wool, or wool-casein unions by impregnation with a dye of low affinity under the conditions of impregnation followed by a treatment whereby the liquid medium is evaporated only from certain parts of the fabric. By using resins, such as cyanamide-formaldehyde, which alter the dyeing properties and effecting local evaporation, similar patterning is produced.<sup>145</sup> Reference has previously been made to methods for dyeing at low temperatures and R. Haynn<sup>146</sup> achieves this for mixtures of wool and cellulose by adding formic acid and sodium sulphate to the bath containing direct dyes; these assistants increase the depth of shade on the wool and cellulose respectively to extents which are roughly proportional to the amounts added. Finally, a discussion of the practical aspects of union dyeing has been published by F. Smith.<sup>147</sup>

R. H. Peters<sup>148</sup> has measured the absorption of acid dyes by nylon and has shown that they combine with the terminal amino- or the imino-groups according to whether the pH of the bath is greater or less than 3. Acetylation of nylon reduces dye affinity but not to the extent expected from the reduced affinity for acids. Other points of interest in the paper are that the dyeings are faster than on wool and that owing to the limited number of sites for the dye it is necessary to mix dyes of equal affinity so that one dye is not excluded by others. The rate of adsorption of direct dyes by nylon has been shown<sup>149</sup> to be increased by small amounts of cationic paraffin-chain salts and explanations based on increased aggregation of dye particles or on complex formation between dye and "catalyst" are proposed. The production of deep shades on nylon can be achieved by a short pretreatment with certain acid solutions, as for instance sulphuric acid of density 1.21, followed by dyeing with direct dyes.<sup>150</sup>

Although of only indirect interest at present, it has been recorded that a wide range of water-insoluble monoazo-dyes may be used for the dyeing of vinyl polymers.<sup>151</sup>

### PRINTING.

J. W. Reidy,<sup>152</sup> in a short paper, has compared the use of basic, acid, mordant, direct, sulphur, vat, and azoic dyes, and of pigments for printing

<sup>144</sup> Courtaulds Ltd., C. M. Whittaker, H. A. Thomas, C. C. Wilcock, and C. P. Tattersfield, B.P. 565,731; B., 1945, II, 58.

<sup>145</sup> *Idem*, B.P. 564,131; B., 1944, II, 357.

<sup>146</sup> *Textilber.*, 1943, 24, 266; B., 1944, II, 356.

<sup>147</sup> *J. Soc. Dyers and Col.*, 1945, 61, 8; B., 1945, II, 81.

<sup>148</sup> *Ibid.*, 95; B., 1945, II, 216.

<sup>149</sup> J. H. MacGregor and C. Pugh, *ibid.*, 122; B., 1945, II, 216.

<sup>150</sup> Tootal Broadhurst Lee Co., Ltd., R. P. Foulds, W. H. Roscoe, and W. H. Watson, B.P. 568,092; B., 1945, II, 179.

<sup>151</sup> Amer. Cyanamid Co., B.P. 568,037; B., 1945, II, 217.

<sup>152</sup> *J. Soc. Dyers and Col.*, 1945, 61, 37; B., 1945, II, 140.



and dyeing, with special reference to cellulose acetate and nylon. G. Hasse<sup>153</sup> has also reviewed methods of printing, especially with organic lake pigments, and has described a recent process in which a binding agent is emulsified in water and used for suspending the pigment. In this process the fixation is effected by heating at about 140° for some two minutes. It is also mentioned that prints on rayon are less resistant to washing than on cotton and that, to avoid weakening of the binders, the alkalinity of the washing water should not be high. Improvement of the affinity of viscose rayon for acid dyes can be effected by using magnesium oxide, a urea-formaldehyde resin, or urea alone in the paste, and there are indications that the animalising of viscose rayon with nitrogen or sulphur compounds also improves the affinity for film-printed acid dyes.<sup>154</sup> W. Meitner<sup>155</sup> has studied the problem of why the presence of urea improves the affinity for acid dyes and concludes that for success, the particle size of the dye must exceed a certain minimum value, the fixation occurring by the formation of dye aggregates within the fibres. Recipes for the satisfactory printing of formaldehyde-treated rayon with various classes of dye have been given by M. Kerth<sup>156</sup> while the new "Orema" printing colours have also been discussed.<sup>157</sup> The latter are finely-divided pigments with no affinity for fibres; they are resistant to washing, to light, and to hot dilute caustic alkali.

Of the patents dealing with improvements in printing the following may be mentioned. Use of heteropoly-acids with basic dyes followed by precipitation of the insoluble lakes on the fibres by means of acids<sup>158</sup>; the production of fast prints from water-soluble dyes by printing in the presence of an acid and thiourea followed by steaming in the presence of formaldehyde<sup>159</sup>; and the printing of viscose rayon with direct or acid colours using compounds  $R \cdot S \cdot CH_2 \cdot CO_2Na$ , where R is an alkyl or benzyl group, as assistants.<sup>160</sup> The use of many binding or film-forming materials under specific conditions has been protected. These include casein,<sup>161</sup> interpolymers of drying oils with styrene, vinyl acetate, or a methacrylic ester,<sup>162</sup> alkyd or urea-formaldehyde resins, rubber, polychloroprene, or cellulose acetate propionate,<sup>163</sup> and ethylcellulose used with polyesters.<sup>164</sup>

In connexion with cellulose ether solutions it has been claimed<sup>165</sup> that by addition of 0.1—2% of the sodium salt of an alkylphenylphenol-polysulphonate the viscosity can be increased tenfold.

<sup>153</sup> *Textilber.*, 1943, **24**, 277; B., 1944, II, 357.

<sup>154</sup> R. Franzoso, *ibid.*, 313; B., 1945, II, 110.

<sup>155</sup> *J. Soc. Dyers and Col.*, 1945, **61**, 33; B., 1945, II, 140.

<sup>156</sup> *Textilber.*, 1943, **24**, 233; B., 1944, II, 357.

<sup>157</sup> E. Krähenbühl, *ibid.*, 315; B., 1945, II, 104.

<sup>158</sup> Calico Printers Assoc., and W. S. Miller, B.P. 566,258; B., 1945, II, 111.

<sup>159</sup> Soc. Chem. Ind. in Basle, B.P. 566,977; B., 1945, II, 141.

<sup>160</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,321,501; B., 1945, II, 180.

<sup>161</sup> Stein, Hall & Co., U.S.P. 2,310,795; B., 1944, II, 317.

<sup>162</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,322,837; B., 1945, II, 218.

<sup>163</sup> Amer. Cyanamid Co., U.S.P. 2,323,871; B., 1945, II, 243.

<sup>164</sup> Atlas Powder Co., U.S.P. 2,188,073; B., 1945, II, 63.

<sup>165</sup> Dow Chem. Co., U.S.P. 2,321,270; B., 1945, II, 178.



## FINISHING.

The literature on water-repellent finishes consists of patents except for one paper<sup>166</sup> dealing with the use of chloromethyl ethers of aliphatic alcohols. The products obtained by their combination with pyridine are effective hydrophobing agents for textiles, provided the alkyl group contains at least sixteen carbon atoms. Among patented processes may be mentioned the use of long-chain fatty acid esters of ethylcellulose as impregnants<sup>167</sup> or of pretreatment with a plasticised cellulose ether or ester followed by reaction with any one of a wide range of long-chain aliphatic etherifying or esterifying agents.<sup>168</sup> The deposition of various metal soaps on the fibre<sup>169</sup> or of metal hydroxides followed by paraffin wax<sup>170</sup> is also suggested. Soft, water-repellent finishes are provided by substituted *NN*-ethyleneureas<sup>171</sup> and by many complex ethers and ether-acids.<sup>172</sup>

Fireproof finishes, judging from recent patents, tend to become increasingly complicated. A. E. Ervine<sup>173</sup> has discussed the uses of chlorinated paraffins in rendering fabrics resistant to fire, water, and mildew; certain chlorinated resins and waxes mixed with zinc carbonate have been suggested for similar purposes.<sup>174</sup> Chlorinated alkyl esters of phosphoric acid, when mixed with melamine-formaldehyde resins, are also reputed to impart flame-damping properties.<sup>175</sup> Variants of the borax-boric acid treatment for loose cotton,<sup>176</sup> and the use of guanidine salts,<sup>177</sup> are claimed, the latter being useful also for extinguishing after-glow.

An authoritative review of the question of mould and bacterial attack of textiles has been published by R. G. Fargher,<sup>178</sup> who states that salicylanilide, *p*-nitrophenol, thiolbenzthiazole, and 5 : 5'-dichloro-2 : 2'-dihydroxydiphenylmethane (G4) are particularly effective in the prevention of growth of micro-organisms on cotton. In this country tendering of open fabrics is due chiefly to chemical modification, but biological attack may become appreciable with heavy fabrics. In hot, humid climates it may be serious for all weights. It is emphasised that trials under actual conditions of use are essential so that the retention of rot-proofing agent as well as its intrinsic efficiency can be assessed. Under conditions of serious contamination copper compounds are preferred to

<sup>166</sup> D. N. Kursanov and V. N. Setkina, *J. Appl. Chem. Russ.*, 1943, **16**, 36; *A.*, 1945, **II**, 4.

<sup>167</sup> Hercules Powder Co., U.S.P. 2,317,499; *B.*, 1945, **II**, 112.

<sup>168</sup> H. Dreyfus, D. Finlayson, and R. G. Perry, B.P. 566,371; *B.*, 1945, **II**, 112.

<sup>169</sup> Hall Laboratories Inc., U.S.P. 2,182,045; *B.*, 1945, **II**, 21.

<sup>170</sup> Pond Lily Co., U.S.P. 2,323,387; *B.*, 1945, **II**, 243.

<sup>171</sup> Gen. Aniline & Film Corp., U.S.P. 2,314,968; *B.*, 1944, **II**, 358.

<sup>172</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,313,742; *B.*, 1945, **II**, 22.

<sup>173</sup> *Amer. Dyestuff Rep.*, 1944, **33**, 189; *B.*, 1945, **II**, 20.

<sup>174</sup> M. Leatherman, U.S.P. 2,326,233; *B.*, 1945, **II**, 305.

<sup>175</sup> Geigy Colour Co., Ltd., and C. Hobday, B.P. 564,573; *B.*, 1945, **II**, 22.

<sup>176</sup> Lockport Cotton Batting Co., U.S.P. 2,185,695; *B.*, 1945, **II**, 22.

<sup>177</sup> H. Dreyfus, B.P. 569,040; *B.*, 1945, **II**, 272.

<sup>178</sup> *J. Soc. Dyers and Col.*, 1945, **61**, 118; *B.*, 1945, **II**, 217.



chromium although they leach out more quickly. However, only chromium compounds can be used with rubber-proofed fabrics, and both are undesirable when drying oils are present. Other authors considering this problem have also proved the value of copper compounds for rot-proofing. For instance, hydrated copper oxide has been chosen after a consideration of various protective treatments,<sup>179</sup> whilst copper dimethylglyoxime has been shown to be superior to copper naphthenate.<sup>180</sup> Patents for the precipitation of copper naphthenate<sup>181</sup> or a copper-cellulose complex<sup>182</sup> have been granted.

The realisation of improved fabric properties by impregnation with synthetic resins commands the usual interest. D. H. Powers<sup>183</sup> has described some effects of finishing with urea-melamine and phenol-formaldehyde resins. Melamine resins did not affect the strength of cotton but increased that of rayons, while urea resins had no effect on the strength of rayons and reduced that of cotton. It seems probable that these results indicate a poor finishing technique rather than unsatisfactory resins. Shrinkage on washing was reduced by the presence of any of the resins. If urea- or cyanamide-formaldehyde resins be applied to cloths required for raising, a fuller nap and an improved handle result.<sup>184</sup> A puckered effect has been obtained by printing with a water-insoluble cellulose ether so that shrinkage in the untreated regions occurs on treatment with caustic alkali.<sup>185</sup> In a comprehensive patent of eight sections, E. I. Du Pont de Nemours & Co.<sup>186</sup> consider the use of esters of methacrylic acid in conjunction with partly saponified polyvinyl acetates, multivalent metal salts, waxes, and natural and synthetic resins for the production of sizes, water-repellent finishes, delustrants, and slip-resistant finishes.

As a variant on the use of formaldehyde the cloth is impregnated with an acid solution of formaldehyde containing casein; on baking to effect reaction between the protein, cellulose, and aldehyde a fabric is obtained which is resistant to washing and abrasion.<sup>187</sup>

Finishing by padding with viscous solutions followed by precipitation of the soluble component has been protected for solutions of nylon in acids<sup>188</sup> and of cellulose in sodium zincate solutions.<sup>189</sup> Long-chain aliphatic alcohols in stable emulsions can be used as scrooping agents.<sup>190</sup>

<sup>179</sup> P. da R. Azevedo and F. J. Maffei, *Anais Assoc. Quím. Brasil*, 1944, 3, 120; B., 1945, II, 11.

<sup>180</sup> A. C. Neish, G. A. Ledingham, and A. G. Mackey, *Canad. J. Res.*, 1945, 23, F, 198; B., 1945, II, 305.

<sup>181</sup> R. H. McKee, B.P. 568,679; B., 1945, II, 272.

<sup>182</sup> C. B. White, U.S.P. 2,186,713; B., 1945, II, 82.

<sup>183</sup> *Ind. Eng. Chem.*, 1945, 37, 188; B., 1945, II, 175.

<sup>184</sup> Courtaulds Ltd., and C. P. Atkinson, B.P. 570,696; B., 1945, II, 305.

<sup>185</sup> Sayles Finishing Plants Inc., U.S.P. 2,319,903; B., 1945, II, 111.

<sup>186</sup> B.P. 563,707; B., 1944, II, 318.

<sup>187</sup> Heberlein & Co. A.-G., B.P. 565,337; B., 1945, II, 82.

<sup>188</sup> Tootal Broadhurst Lee Co., Ltd., R.P. Foulds, W. H. Roscoe, and W. H. Watson, B.P. 567,043; B., 1945, II, 141.

<sup>189</sup> S. M. Edelstein, U.S.P. 2,322,427; B., 1945, II, 213.

<sup>190</sup> Richards Chem. Works Inc., U.S.P. 2,190,331; B., 1945, II, 180.



With the present interest in infra-red drying a review of the subject by F. L. Atkin<sup>191</sup> should be valuable. The economic advantage of gas-heated units is stressed.

J. Kirkwood<sup>192</sup> has reviewed the application of synthetic rubbers by rubber-coating machinery. It has been found<sup>193</sup> that the sum of the copper and manganese present in rayon to be used for rubberising should not exceed 0.005%, although cobalt, chromium, iron, and fatty acids are not important. Coated waterproofed fabrics can be produced with a plasticised mixture of nitrocellulose and alkyd resin<sup>194</sup> or with oil-modified alkyd resins alone,<sup>195</sup> whilst for protective industrial fabrics it is suggested that this type of coating has now been replaced by polyvinyl chloride or butyral, or by Neoprene.<sup>196</sup> A review of the value of acrylic resins for the coating of textiles has been made by H. Lachmann.<sup>197</sup>

#### ANALYSIS AND TESTING.

The value of a viscosity test for the assessment of damage in textiles has been further stressed,<sup>198</sup> and data are given showing the damage to cotton produced by bleaching, hydrolysis, or washing. W. O. Hisey and C. E. Brandon<sup>199</sup> report favourably on the use of the Hoeppler falling-ball viscometer for measuring the viscosity of wood pulps in cuprammonium. The error is stated to be half that of the standard TAPPI test and a method of obtaining dissolution of the cellulose in five minutes is given. The recent preference for cupriethylenediamine as a solvent, especially for pulps, has been further stressed<sup>200</sup> and routine methods are described. Details of a rather involved tumbling device for the preparation of solutions for fluidity determination have also been given.<sup>201</sup> In their second paper on the fluidity of nylon solutions, J. Boulton and D. L. C. Jackson<sup>202</sup> conclude that *m*-cresol is to be preferred to formic acid as a solvent for routine use, and they present further data on the fluidity of nylon degraded photochemically or by acid. A critical discussion of the theory of fluidity measurements for estimating fibre damage has been submitted by De Voorzorg.<sup>203</sup>

Several useful papers concerned with the analysis of cellulose esters are now available. S. N. Danilov<sup>204</sup> has considered methods for determining the reducing power, the degree of oxidation of a hydrocellulose,

<sup>191</sup> *Gas J.*, 1944, **244**, 371, 402, 407, 413, 415; B., 1945, I, 1.

<sup>192</sup> *Trans. Inst. Rubber Ind.*, 1944, **20**, 110; B., 1945, II, 110.

<sup>193</sup> P. Kluckow and Kehren, *Textilber.*, 1943, **24**, 84; B., 1945, II, 110.

<sup>194</sup> Columbus Coated Fabrics Corp., U.S.P. 2,188,901; B., 1945, II, 141.

<sup>195</sup> Lustrafil Ltd., and G. L. Godman, B.P. 563,586; B., 1944, II, 318.

<sup>196</sup> J. R. Owens, *Off. Digest*, 1944, No. 236, 261; B., 1944, II, 364.

<sup>197</sup> *Textilber.*, 1943, **24**, 362; B., 1945, II, 20.

<sup>198</sup> O. Eisenhut and H. Vetter, *Textilber.*, 1941, **22**, 424; *Chem. Abs.*, 1944, 2212.

<sup>199</sup> *Paper Trade J.*, 1945, **120**, *TAPPI Sect.*, 11, 21; C., 1945, 106.

<sup>200</sup> R. M. Levy, P. Muffat, and W. D. Harrison, *ibid.*, 1944, **118**, *TAPPI Sect.*,

45. A. J. Corey, *ibid.*, 167; B., 1944, II, 278; C., 1944, 119.

<sup>201</sup> S. A. Simon, *Text. Res. J.*, 1945, **15**, 82.

<sup>202</sup> *J. Soc. Dyers and Col.*, 1945, **61**, 40; B., 1945, II, 135.

<sup>203</sup> *Textilber.*, 1943, **24**, 355; B., 1945, II, 12.

<sup>204</sup> *Trans. All-Union Conf. Anal. Chem.*, 1944, **3**, 204; C., 1945, 25.



and the degree of xanthation in a viscose solution. The total acyl content of various aliphatic esters of cellulose has been determined by a method involving alkaline saponification in solution.<sup>205</sup> This method is accurate and is an extension of the similar valuable work of this group of authors.

C. M. Conrad<sup>206</sup> has critically reviewed methods for the determination of the wax content of cotton, and has proposed a method in which sugars and waxes are extracted with hot 95% alcohol, which is then mixed with chloroform, when by suitable dilution with water, phase separation occurs with the sugars and wax in separate layers.

The analysis of textile fibre mixtures by shaking with a liquid of density intermediate between that of the two components is well known. R. Lassé<sup>207</sup> gives detailed instructions for a modified form of this method including the selective deposition of heavy metals on fibres to enhance the density differences. In the only other experimental paper on this subject three methods for finding the content of cotton in asbestos textiles are described.<sup>208</sup> For calculations in connexion with the analysis of mixture of fibres, W. Bobeth<sup>209</sup> has determined moisture regains at 65% relative humidity for various fibres and recommends that his figures should replace standard regains for this purpose.

As a test for preservation against attack by micro-organisms H. J. Bunker<sup>210</sup> finds that determination of the rotting times of fabrics buried in soil containing 20% of water at 30° gives results agreeing with the method of burying the treated fabric in the open and finding the number of controls it outlives. A volumetric estimation of mercury when used in mildew-proofing compounds has been described.<sup>211</sup> G. Becker<sup>212</sup> has discussed, with experimental data, the attack of rayons and cotton by termites and suggests that a fabric is termite-resistant if there is little or no visible attack on a 5 × 10-cm. sample by 120 insects (of a definite type) after eight weeks under tropical conditions.

O. Mecheels<sup>213</sup> has described testing methods for cloths given rainproof finishes. Heat-insulation properties and resistance to rain and sweat evaporation are included; results show wide scatter due to irregularities in the finish, but for the water-penetration test they follow a Gaussian distribution curve. Also concerned with the properties of rayon staple-wool mixtures which have been waterproofed is a paper<sup>214</sup> which shows that the usual tests of physical properties do not necessarily represent

<sup>205</sup> C. J. Malm, L. B. Genung, R. F. Williams, jun., and M. A. Pile, *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 501; C., 1945, 25.

<sup>206</sup> *Ibid.*, 745; C., 1945, 105.

<sup>207</sup> *Textilber.*, 1943, **24**, 466; B., 1944, II, 351.

<sup>208</sup> Anon., *Asbestos*, 1944, **25**, No. 11, 12; C., 1944, 169.

<sup>209</sup> Klepzig's *Textil-Z.*, 1941, **44**, 975; *Chem. Abs.*, 1944, 2212.

<sup>210</sup> *Proc. Soc. Agric. Bact.*, 1943, 9; C., 1944, 169.

<sup>211</sup> D. A. Shiracfi, *Amer. Dyestuff Rep.*, 1944, **33**, 310; C., 1945, 4.

<sup>212</sup> *Textilber.*, 1942, **23**, 523, 573; C., 1945, 24.

<sup>213</sup> *Ibid.*, 1943, **24**, 26; C., 1945, 105.

<sup>214</sup> J. Stadler and B. Hartmark, *ibid.*, 311; B., 1945, II, 110.



behaviour in practice. As an illustration, it is stated that in the Bundesmann rain test less water is absorbed by treated materials, but on drying they also lose water less rapidly than ordinary cloths.

The clamminess of moist fabric when in contact with the body has been investigated with 36 knit fabrics of various structures, weights, and fibre types.<sup>215</sup> Three tests, including a subjective test, were used and gave similar results, showing that the chilling was least with 100% wool and increased with increasing cotton content, while all rayons, which were similar, had a much greater chilling effect than that of a 50 : 50 wool-cotton fabric. Terry-stitch knitting corresponded to the smallest initial temperature fall and rib or flat knitting to the greatest. A study has also been made<sup>216</sup> of the thickness, compressibility, thermal transmission, air-permeability, breaking strength, and washing-shrinkage of 156 blankets composed of wool, cotton, rayon, and mixtures of these. The effects of various combinations of laundering, dry-cleaning, napping, and abrasion are also given. For all blankets the thermal transmission is independent of the type of fibre and is governed by the thickness. The above papers are excellent examples of the recent movement towards the study of the behaviour of fabrics in use by means of adequate and controlled experiments.

H. Böhringer<sup>217</sup> has characterised wool and rayons in terms of microscopical data, frequency curves of fibre width or staple, swelling capacity, and whiteness and gloss. The same author<sup>218</sup> has also given results for the strength, extensibility, elasticity, crimp, resistance to bending and twisting, water absorption, and density of wool, casein, and viscose and acetate rayons.

The Textile Institute has proposed comprehensive standard testing methods for narrow fabrics.<sup>219</sup> These include all general physical properties, testing for metals, rot-proofing agents and other chemicals, and various colour-fastness tests. Of interest to those concerned with the theory of testing for fibre strength is a mathematical work by H. E. Daniels,<sup>220</sup> who derives a relation between the strength of a bundle of threads and of its constituent fibres.

It has been shown<sup>221</sup> for samples of wool, cotton, silk, and flax that the Müller formula for moisture content does not hold for fibres under natural, that is, changing atmospheric conditions.

The suitability of circular- and warp-knitted rayon fabrics for raising has been discussed<sup>222</sup> with the help of photomicrographs.

<sup>215</sup> C. W. Hock, A. M. Sookne, and M. Harris, *J. Res. Nat. Bur. Stand.*, 1944, 32, 229; B., 1945, II, 12.

<sup>216</sup> H. F. Schiefer, H. T. Stevens, P. B. Mack, and P. M. Boyland, *ibid.*, 261; B., 1945, II, 54.

<sup>217</sup> *Textilber.*, 1943, 24, 59; C., 1945, 103.

<sup>218</sup> *Ibid.*, 117; B., 1945, II, 105.

<sup>219</sup> Anon., *J. Text. Inst.*, 1944, 35, s7; C., 1945, 23.

<sup>220</sup> *Proc. Roy. Soc.*, 1945, A, 183, 405; B., 1945, II, 299.

<sup>221</sup> W. B. Schaponschnikow, *Textilber.*, 1943, 24, 120; B., 1945, II, 105.

<sup>222</sup> R. Lassé, *ibid.*, 1944, 25, 97, 133; B., 1945, II, 13.



## PULP AND PAPER.

BY JULIUS GRANT, M.Sc., Ph.D., F.R.I.C.

THE outstanding events of the last year have necessarily exerted a major influence on the course of an industry so susceptible to variations in war-time conditions. The most important change has been the gradual increase in wood pulp supplies from abroad, particularly from Sweden, but also from Finland. Their arrival in the late summer, together with the increased quotas of wood pulp allowed to manufacturers by the Paper Control, provided a very welcome concession, and the first sign of a return to peace-time conditions. Unfortunately, however, a paper shortage still exists, and the lack of priority (particularly as regards labour) from which the industry suffers has aggravated the position.

In addition, there has been a very serious diminution in the supplies of waste paper, which were one of the mainstays of the industry during the critical years. This is perhaps understandable in view of the official attitude towards other forms of salvage (e.g., metal and rubber) which are now no longer needed, but it is hoped that it is not too late to re-arouse public interest. There seems little likelihood of the re-appearance of esparto grass in quantities approaching pre-war consumption in the near future. The rate of exchange and the shipping position are the principal factors opposing its return, an unfortunate situation in view of the export value of esparto papers.

A forecast<sup>1</sup> has been made, in the United States, of the world pulp and paper positions for the next few years. It indicates that deficits in world paper requirements are likely to occur in the immediate post-war years period, but that by 1948 the position should have been more than rectified, despite the increasing consumption that is likely to occur, in the United States at any rate. On the European continent recovery may be fairly rapid. Except in Germany, losses of mills and machinery have not been great, but the fuel shortage is the principal handicap. In Sweden, in particular, this difficulty has been overcome temporarily by the use of wood, but in any case, Sweden has had available for some time considerable stocks of both pulp and paper for export to the remainder of Europe and to the United States. These, and the lesser sources of supply now becoming available, should help to bridge any gap between the present general world shortage and the resumption of full peace-time production. An interesting review of present Swedish methods and war-time expedients comes from E. C. Jahn.<sup>2</sup>

<sup>1</sup> Anon., *Paper Trade J.*, 1945, 120, No. 5, 18.

<sup>2</sup> *Ibid.*, *TAPPI Sect.*, 168; B., 1945, II, 239.



## PULPING PROCESSES.

*Raw Materials.*—The possibilities of the papermaking materials of the British Empire are the subject of a paper by J. R. Furlong and E. L. Hill<sup>3</sup>; they deal with wood, bamboo, grasses, reeds, nettles, yawa fibre, and textile and cordage wastes. J. R. Furlong (with H. E. Coomber)<sup>4</sup> also records that a bleachable pulp, reasonably free from shive, and suitable as a cheap "filler fibre" for opacifying printings or writings, is obtainable from the Nigerian grass, *Vossia cuspidata*; the digestion conditions are somewhat more drastic than those commonly used for straw. Users of straw will be interested in a comparison of the different cereal straws (H. C. Koch<sup>5</sup>). This refers only to straw for paperboard manufacture, but it establishes clearly that the most important point of difference is in the drainage rates of the resulting pulps; combine winter wheat pulp has the highest and barley pulp the lowest value.

*Mechanical Process.*—A novel chemical method of de-barking trees prior to pulping is described by J. D. Hale.<sup>6</sup> The reagent (preferably a mixture of caustic soda and arsenic oxide) is applied, as a paste, to a strip of freshly-exposed sapwood in the spring; this kills the tree at a stage such that peeling long after the normal peeling period is possible. The so-called semi-chemical methods (which are equally appropriately termed "semi-mechanical" methods) appear to be increasing in both number and variety; products of relatively high strength (e.g., suitable for the manufacture of roofing felts and boards) are now obtainable. In a method described by G. A. Ritter,<sup>7</sup> yields of 75—85% are obtained by treating wood chips from a screw press with steam and/or chemicals, in a series of zones produced by horizontal pipes arranged vertically in series and containing screw conveyors; an Asplund defibrator may conveniently be used. The product is finished in a disc-type refiner.

Although birch mechanical wood pulp has a shorter fibre and lower bursting strength and freeness than regular mechanical wood pulp, L. G. Sears<sup>8</sup> finds that the inclusion of up to 20% in a newsprint furnish produces no appreciable reduction in the quality of the paper, so long as the original moisture content of the wood is not too low. D. H. Kincaid's comparison<sup>9</sup> of mechanical wood pulps from regular, mixed, and top woods shows that top wood gives satisfactory results, despite its shorter fibre and greater freeness.

*Sulphite Process.*—The relative merits of direct and indirect cooking methods are assessed by V. P. Edwardes,<sup>10</sup> who finds advantages in the latter by reason of improved acid penetration and freedom from dilution

<sup>3</sup> *Bull. Imp. Inst.*, 1944, 42, 232; B., 1945, II, 136.

<sup>4</sup> *Ibid.*, 149; B., 1945, II, 14.

<sup>5</sup> *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 135; B., 1945, II, 211.

<sup>6</sup> *Pulp and Paper Mag. Canada*, 1944, 45, 615; B., 1945, II, 14.

<sup>7</sup> *Ibid.*, 1945, 46, 528; B., 1945, II, 266.

<sup>8</sup> *Ibid.*, 185; B., 1945, II, 175.

<sup>9</sup> *Ibid.*, 155; B., 1945, II, 175.

<sup>10</sup> *Ibid.*, 1944, 45, 891; B., 1945, II, 77.



by condensed steam; in order to secure them, however, it is essential that the chips are properly packed in the digester, *i.e.*, they should lay flat and uniformly distributed across it. Economies in steam and chemicals and an improved yield and general pulp quality are also recorded for the system of forced circulation through external heaters described.

The relative merits of magnesium bisulphite as compared with calcium bisulphite as a cooking reagent have often been discussed, but G. H. Tomlinson's method<sup>11</sup> of using the former in the interests of by-product recovery should be an added point in its favour. Thus the resulting waste liquors may be evaporated without scale formation, and the magnesium oxide and sulphur dioxide so produced recombined, in presence of water, to form a cooking liquor containing magnesium sulphite and bisulphite. Alternatively, the evaporated liquor may be neutralised and fermented, or treated for the recovery of vanillin, before it is burned. F. B. Schelhorn<sup>12</sup> has also studied recovery methods as applied to the monosulphite process, and finds that cooks made with liquors similar in composition to recovered waste liquors from this process are less effective than the corresponding fresh liquors. This difference appears to originate at the sulphiting stage rather than in the smelting operation, and probably is associated with the reaction between sulphur and sulphur dioxide in presence of carbonates.

*Alkaline Processes.*—The suitability of 22 varied woods from the S.E. United States for the dual purposes of tannin extraction and conversion of the residue into kraft pulp was investigated by L. V. Forman.<sup>13</sup> Carolina red maple and Australian pine give the most promising results, and it is interesting to note that species having no tannin in the bark or wood yield pulps of low strength characteristics. S. D. Wells<sup>14</sup> found that typical kraft pulps are obtainable from scrub pine wood by replacing some 50% of the sodium sulphide in the liquor by sodium sulphite, and increasing slightly the cooking time and temperature. Heat recovery is improved, and the odour nuisance lessened, for a small additional cost of make-up chemical.

Automatic digester control for the alkaline process appears to have at length been achieved, *viz.*, by the Foxbro system described by H. O. Ehrisman.<sup>15</sup> It is an electronic type, resistance-bulb instrument, having a very rapid dynamic response and a high temperature-sensitivity; it may be used to record the temperatures at specified zones in the digester, and to control the uniformity of circulation of the liquor and the operating and relief pressures.

Three papers dealing with the recovery process are of special note. H. F. Lewis<sup>16</sup> describes the Goodell process, in which evaporated kraft

<sup>11</sup> *Pulp and Paper Mag. Canada*, 817; B., 1945, II, 55.

<sup>12</sup> *Paper Trade J.*, 1944, 119, *TAPPI Sect.*, 223; B., 1945, II, 106.

<sup>13</sup> *Ibid.*, 118, *TAPPI Sect.*, 97; B., 1944, II, 312.

<sup>14</sup> *Ibid.*, 119, *TAPPI Sect.*, 137; B., 1945, II, 15.

<sup>15</sup> *Ibid.*, 195; B., 1945, II, 54.

<sup>16</sup> *Ibid.*, 1945, 120, *TAPPI Sect.*, 201; B., 1945, II, 267.



black liquor is spray-dried, the product being subjected to destructive distillation, and then discharged into an ordinary recovery furnace. The non-condensable gases are a source of heat, and from the tar separated from the aqueous distillate are derived "phenolic oils" containing phenols, including guaiacol and cresols. The aqueous fraction contains methyl alcohol, acetone, and methyl acetate. The use of synthetic salt cake (made by fusing together sulphur and sodium carbonate), as described by V. Woodside, J. D. MacMahon, and G. P. Vincent,<sup>17</sup> enables an increased furnace throughput, economies of sulphur and furnace fuel, ease of control, a clear white liquor, and improved sedimentation to be achieved; moreover, since it need not be smelted and is readily soluble, it can be added to the green liquor instead of to the black liquor. The third paper, by E. A. Harper,<sup>18</sup> is of interest because it specifies the optimum conditions for the conversion of carbonate sludge from the recovery process into lime; plant to handle 35 tons per day is described.

Lignin is the subject of papers by J. Seiberlich<sup>19</sup> and by F. E. Brauns, H. F. Lewis, and E. B. Brookbank.<sup>20</sup> The former describes how a water-resistant wallboard may be made by moulding (at 171° for 3 minutes) purified waste lignin derived from the Scholler wood saccharification process. The latter deals with lignin from waste alkali hardwood liquor (Meadol); a number of esters and ethers were prepared, after purification of the lignin by precipitation as a lead compound.

*Testing Methods.*—New or revised TAPPI standard methods which have appeared are: T14 sm-44<sup>21</sup> (dirt in wood chips); T15 m-45<sup>22</sup> (ash in wood); T468 m-45<sup>23</sup> (water-soluble sulphates and chlorides in pulp); T449 m-45<sup>24</sup> (bacteriological examination of pulp and slush stock); T16 sm-45<sup>25</sup> (sieve analysis of wood chips); T611 m-44<sup>26</sup> (analysis of bleaching powder, bleach liquor, and bleach sludge). W. O. Hisey and C. E. Brandon<sup>27</sup> suggest improvements in the TAPPI method (T206 m) for the determination of the cuprammonium viscosity of cellulose, the principal of which is the use of a Hoeppler viscometer. Advantages are that a low concentration of pulp and a large falling ball may be used (thereby increasing the accuracy), and that the same solution may be tested several times. A disadvantage is that the dispersion has to be made separately and transferred to the viscometer, although working in an inert gas is unnecessary.

A useful tool for rapidly punching wedges out of wet lap pulp when

<sup>17</sup> *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 29; B., 1945, II, 176.

<sup>18</sup> *Ibid.*, 81; B., 1945, II, 211.

<sup>19</sup> *Chem. Industries*, 1945, 56, 53; B., 1945, II, 136.

<sup>20</sup> *Ind. Eng. Chem.*, 1945, 37, 70; B., 1945, II, 136.

<sup>21</sup> *Paper Trade J.*, 1944, 118, *TAPPI Sect.*, 117; C., 1945, 25.

<sup>22</sup> *Ibid.*, 1945, 120, *TAPPI Sect.*, 121; C., 1945, 170.

<sup>23</sup> *Ibid.*, 121, *TAPPI Sect.*, 41; C., 1945, 242.

<sup>24</sup> *Ibid.*, 28; C., 1945, 241.

<sup>25</sup> *Ibid.*, 106; C., 1945, 241.

<sup>26</sup> *Ibid.*, 120, *TAPPI Sect.*, 141; C., 1945, 160.

<sup>27</sup> *Ibid.*, 11, 21; C., 1945, 106.



sampling for moisture tests is described by W. O. Manor.<sup>28</sup> L. E. Wise<sup>29</sup> combines methods for the isolation and determination of hemicelluloses in coniferous woods. The ground sample is treated with a solution of sodium hypochlorite in acetic acid at 30° for 24 hours (to remove lignin). The hemicelluloses are then dissolved out in potassium hydroxide solution in an atmosphere of nitrogen, reprecipitated with acetic acid, freed from residual lignin by bromination, and washed, dried, and weighed.

#### PAPER MANUFACTURE.

*Beater Operations.*—Considerable interest has been aroused by a notable contribution from the laboratories of Imperial Chemical Industries Ltd. (E. Fajans, F. Hamilton, F. North, and H. Samuels<sup>30</sup>). Pulp was milled at a high consistency, under conditions which produced high internal friction; extreme fibrillation resulted, but little strength was developed. The continuation of such milling in presence of certain cellulose derivatives and natural gums (which, used alone, produced no strength increase) resulted in strength properties of the same order as those of a beaten pulp. Advantages claimed, as compared with ordinary beating, are a considerable economy in power and, in some cases, improved control of the beating process. These claims aroused some controversy as to whether the results could be reproduced on the large scale, and whether the new method is a complete substitute for the classical beater. Further work will clarify these points, but the outstanding interest of the method and its potential value as a tool for investigating the mechanism of beating are without question.

Other work on beater additives includes an interesting paper by L. C. Haffner and K. A. Kobe<sup>31</sup> on diatomaceous earth as a filler for newsprint, in which (as compared with other fillers) it produces improved printability, retention, opacity, and brightness, but less reduction in strength properties, and a discussion on the rôle of alumina in the mechanism of sizing by J. C. Redd.<sup>32</sup> It is shown that the activity as an absorbent for arsenious oxide of the "alumina" precipitated from aqueous solutions of aluminium salts may be correlated both with its ability to size paper pulp, and with the ease with which it peptises to a colloidal sol. The results indicate further that inactivated alumina is absent under normal beater conditions. Since no acidity is developed, colloidal alumina used for the rosin sizing of paper pulp results in improved strength values. Applications of these principles to the use of a protein-rosin size are described. The use of starch in the beater is now well established, although war-time restrictions have precluded it in this country for several years. The mechanism of its action is the subject of a paper

<sup>28</sup> *Paper Trade J.*, 1944, **119**, *TAPPI Sect.*, 63; C., 1945, 26.

<sup>29</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 63; C., 1945, 106.

<sup>30</sup> B.P. 566,143; B., 1945, II, 79. *Proc. Tech. Sect. Paper Makers' Assoc.*, in press.

<sup>31</sup> *Pulp and Paper Ind.*, 1945, **19**, 49; B., 1945, II, 177.

<sup>32</sup> *Paper Trade J.*, 1944, **119**, *TAPPI Sect.*, 66; B., 1944, II, 354.



by R. W. Kerr and N. F. Schink,<sup>33</sup> who find that of the principal saccharide constituents present, the branched-type polymer (amylopectin) is more effective than the linear polymer (amylose) for improving the strength of the paper. The former is probably held mechanically (following adsorption or precipitation) on the fibre, whilst the latter is unable to form a continuous film. Reference should also be made to A. P. Adrian's method<sup>34</sup> of evaluating the opacifying powers of a pigment by depositing it centrifugally, as a film, on a backing of ethylcellulose, which may subsequently be removed and tested optically.

There have also been numerous additions to the growing literature on the production of water-resistance and wet strength by additions to the beater. H. L. Levin<sup>35</sup> claims to have solved the problem of adding asphalt to pulp at room temperature by blending it with a finely-divided, non-fibrous filler, until a friable mixture is obtained. However, most of the work in this sphere deals with resins, particularly of the melamine type, and it is hoped that these materials will soon become available in this country in quantities which will enable confirmatory experiments to be made. Thus K. W. Britt,<sup>36</sup> in a general study of the factors affecting wet strength, compares urea- and melamine-formaldehyde resins and glue-treated papers which have been hardened by heat or formaldehyde, i.e., as an after-process. The effects produced appear to depend largely on the pH. Melamine is better than urea, but both types of paper lose wet tensile strength at a low pH; formaldehyde-hardening is less effective, although independent of the pH, whilst heat-hardened paper (although resistant up to pH 7) loses strength under alkaline conditions. According to G. E. Fromm,<sup>37</sup> melamine improves both the dry and wet tensile and bursting strengths and the dry rub-resistance, but is without effect on the absorbency of unsized sheets. Fromm deals also with factors influencing the efficiency of melamine treatment, and possible applications of the resulting products.

*The Paper Machine.*—A study by G. E. Haeger and U. Söderlund<sup>38</sup> of the adhesion of the pulp sheet to the press felt of a board machine contains a method of evaluating this tendency in terms of the weight of 1 sq. m. of the sheet at the moment that it falls from the felt by reason of its weight increase. Adhesion increases with a rise in the degree of beating, machine speed, sulphite wood content, and with a fall in couch pressure; sizing, consistency, and the difference in levels inside and outside the vat have no effect. D. S. Davis<sup>39</sup> has constructed a useful nomograph for converting machine speeds into production rates, and a Tentative Standard Method (E203 p-44) of calculating machine drying-rates has

<sup>33</sup> *Paper Trade J.*, 1945, 120, No. 25, 86; B., 1945, II, 301.

<sup>34</sup> *Ibid.*, 1944, 119, *TAPPI Sect.*, 149; C., 1945, 27.

<sup>35</sup> U.S.P. 2,190,034; B., 1945, II, 179.

<sup>36</sup> *Paper Ind.*, 1944, 26, 37; B., 1944, II, 313.

<sup>37</sup> *Pulp and Paper Mag. Canada*, 1945, 46, 157, 164; B., 1945, II, 177.

<sup>38</sup> *Svensk Papperstidn.*, 1944, 47, 439.

<sup>39</sup> *Paper Ind.*, 1944, 26, 728; B., 1944, II, 136.



been published by TAPPI.<sup>40</sup> E. W. Holland, C. Brown, and H. A. Harrison<sup>41</sup> have made the interesting observation, covering a wide range of paper furnishes, substances, and wetnesses, that the wetness values of papers after disintegration by the standard (P.M.A.) method and of the machine chest stock from which they were made is usually within the limits of the normal experimental error of the wetness test. The maximum deviations occur with papers of high straw content, but do not exceed 7° S.R. The method cannot be applied to papers which do not disintegrate completely under the specified conditions.

The increased attention now being given to slime control by chemical disinfectants should be recorded, although it is not clear to what extent such methods are preferable to the well-established chlorination processes. However, J. R. Sanborn<sup>42</sup> classifies slime-producing micro-organisms formed in pulp and paper mills according to their resistance to disinfectants; *Aerobacter* are the most prevalent. Of 130 substances tested, 25 (mostly chlorinated phenols and their metal salts and alkyl derivatives) showed promise, but it is pointed out that once slime has grown it may protect the organisms which produce it. Prevention (by cleanliness), however, is, as always, better than cure. Similar tests by G. King<sup>43</sup> give preference to the organic mercurials, whilst J. W. Appling and J. F. McCoy<sup>44</sup> favour Merfenel, with Lignasan as second. These last authors describe a Petri-plate technique for evaluating such disinfectants in terms of the minimum concentrations necessary to inhibit the growth of *Aerobacter aerogenes*. A plate method for the bacteriological examination of mill process water is also used in a TAPPI Tentative Standard (T631 m-45).<sup>45</sup>

Factors influencing the strength of paper was the subject of a symposium organised by the Technical Section of the Paper Makers' Association. E. R. Gibbon<sup>46</sup> and T. H. Farebrother<sup>47</sup> dealt with the tensile load ( $L$ )-stretch ( $S$ ) curves of paper and board, respectively. In general, both sets of results agree, and for paper the expression  $S = F(L^2 + 5L)$  fits the data moderately well (where  $F$  depends on the type of paper). The graphs obtained on recovery from the stretching of paper are approximate inversions of the rising tracks. Farebrother points out that the time factor should be taken into account in assessing such curves, and that studies of this kind are likely to be of significance in letterpress printing, where permanent embossing may occur. A contribution from S. R. H. Edge,<sup>48</sup> though dealing with laboratory-made sheets, is of practical interest, because it shows that the drying of paper under

<sup>40</sup> *Paper Trade J.*, 1944, **119**, TAPPI Sect., 21; B., 1944, II, 313.

<sup>41</sup> *Proc. Tech. Sect. Paper Makers' Assoc.*, 1944, **25**, 270; B., 1945, II, 339.

<sup>42</sup> *Paper Trade J.*, 1944, **119**, TAPPI Sect., 243; B., 1945, II, 106.

<sup>43</sup> *Pacific Pulp and Paper Ind.*, 1944, **18**, June, 39; B., 1945, II, 106.

<sup>44</sup> *Paper Trade J.*, 1944, **119**, TAPPI Sect., 112; B., 1945, II, 15; C., 1945, 27.

<sup>45</sup> *Ibid.*, 1945, **121**, TAPPI Sect., 43; C., 1945, 270.

<sup>46</sup> *Paper Maker*, 1944, **108**, ts 53; B., 1945, II, 56.

<sup>47</sup> *Proc. Tech. Sect. Paper Makers' Assoc.*, 1944, **25**, 216; B., 1945, II, 340.

<sup>48</sup> *Ibid.*, 210; B., 1945, II, 310.



conditions which prevent shrinkage increases the bursting and tearing strengths and wet expansion but lowers the breaking strength. F. J. Greenane<sup>49</sup> extracted wood pulps with alkali (to remove the hemicelluloses) and fractionated the soluble portions by acidification and precipitation with alcohol; in general, the strength increases with increasing uronic acid and xylan contents of the pulp.

*After-Processes.*—R. T. Nazzaro<sup>50</sup> studied GR-S (synthetic rubber) latex as a saturant for paper, and found that the resulting products retain their flexibility on ageing better than if rubber is used; at low temperatures GR-S is preferable to plastics. The tearing strengths of such papers are closer to those produced by the use of natural rubber than by plastics. Disadvantages are a poor tensile strength (although superior to that of papers containing plastics), slow vulcanising rate, poor film tearing-resistance, and limited compatibility with reinforcing plastics. Plastics continue to figure prominently in the literature of after-processes, the special features of melamine-paper laminates (namely, high resistance to abrasion, solvents, and heat) being emphasised by R. H. Malamphy.<sup>51</sup> Moreover, 3% of melamine on the weight of paper (applied from an alcoholic solution) has no appreciable effect on absorbency or flexibility, but the wet strength is then 60% higher than the dry strength, and the dry tensile and folding strengths are improved. G. Alexander<sup>52</sup> is more concerned with the papers used for laminating. Rag papers give the best results because of their high wet strengths, colour, and saturating properties.  $\alpha$ -Pulps are good, but have poor wet strengths and only fair mechanical properties. Kraft papers are cheapest, and good in all respects except colour.

H. T. Barker<sup>53</sup> refers to the use of polyvinyl-base adhesives for laminating weatherproof boards. However, asphalt duplex liners provide the cheapest and simplest means of producing high wet strengths without loss of rigidity in the wet state. An acid starch heated at 90°, cooled, and mixed with 5–20% of a urea-formaldehyde resin also gives good results. A brief survey of the development and future possibilities of the V-types of waterproof solid fibreboard is included. A TAPPI standard method (T630 m-45)<sup>54</sup> for the determination of the m.p. of paraffin wax used for impregnating has appeared.

## PAPER TESTING.

*Strength Tests.*—New TAPPI (tentative) methods for container boards are: a puncture test (T803 m-44)<sup>55</sup> (based on the distance of travel of a falling pendulum carrying a puncturing point, after it has punctured

<sup>49</sup> *Proc. Tech. Sect. Paper Makers' Assoc.*, 1944, **25**, 224; B., 1945, **II**, 340.

<sup>50</sup> *Paper Trade J.*, 1944, **119**, TAPPI Sect., 131; B., 1945, **II**, 15.

<sup>51</sup> *Ibid.*, 134; B., 1945, **II**, 15.

<sup>52</sup> *Ibid.*, 1945, **120**, TAPPI Sect., 233; B., 1945, **II**, 267; C., 1945, 171.

<sup>53</sup> *Ibid.*, 117; C., 1945, 171.

<sup>54</sup> *Ibid.*, 133; C., 1945, 203.

<sup>55</sup> *Ibid.*, 44; C., 1945, 107.



the specimen); and a test (T469 sm-45)<sup>56</sup> for flexural resistance (in which the force required to rupture the horizontal sample strip by means of an inverted stirrup is measured in a tensile strength tester). The TAPPI bursting strength test (T403 m-41)<sup>57</sup> has been modified; the area ruptured is now 1.20 in. in diameter, and the application of a hydrostatic bursting pressure at a controlled increasing rate is introduced.

A particularly interesting and novel contribution to studies of the mechanism of the bursting strength test is provided by the results of high-speed cinematography (up to 2500 exposures per sec.) recorded by H. A. Harrison and G. F. Underhay.<sup>58</sup> The tentative conclusion is reached that the bursting strength is influenced more by the strength and stretch in the machine direction than by those in the cross direction. Reference to the symposium on factors influencing paper strength is made above.<sup>46-49</sup>

P. W. Codwise<sup>59</sup> describes the Howard Smith instrument for determining the erasing properties of paper. A cross-hatched line, drawn under standard conditions on the sample, is subjected to rubbing under standard conditions by one of a series of grit abrasive cloths. In assessing results the time to achieve complete erasure, the amount of fibres removed, and the nature of the resulting surface are all taken into account.

*Penetration and Sizing Tests.*—TAPPI Tentative Method T466 m-44<sup>60</sup> standardises the classical, but little used, test for "sizing" in terms of the rate and extent of curl of a right-trapezoidal specimen of paper floating on water. T467 m-45<sup>61</sup> describes the measurement of the absorptiveness of paper for paraffin wax, by placing it between sheets of blotting paper (which have previously been saturated with the wax) and ascertaining the increase in weight after subjecting the "sandwich" to 105° for 1 hour. The TAPPI method<sup>62</sup> for measuring the air-resistance of paper (T460 m-43) has been modified slightly.

The pen-and-ink sizing test still remains a popular qualitative method for rapid mill work, but, as B. W. Smith<sup>63</sup> points out, it is open to serious error, owing to the great variations in the penetrating powers of modern inks as compared with (*e.g.*) the TAPPI standard ink. It is, therefore, advisable to include in the test also red, green, and violet inks, free from and containing various quantities of a surface-active material; absence of feathering by inks containing 0.5% of this may be regarded as satisfactory. A ball-pointed nib should be used, to make a right-angled X, each arm of which is at 45° to the grain of the paper. The application of the standard dry indicator test to paper containing an internal layer

<sup>56</sup> *Paper Trade J.*, 1945, 121, TAPPI Sect., 11; C., 1946, 90.

<sup>57</sup> *Ibid.*, 1944, 118, TAPPI Sect., 159; C., 1945, 170.

<sup>58</sup> *Proc. Tech. Sect. Paper Makers' Assoc.*, 1944, 25, 273; B., 1945, II, 339.

<sup>59</sup> *Paper Trade J.*, 1945, 120, TAPPI Sect., 73; C., 1945, 107.

<sup>60</sup> *Ibid.*, 1944, 119, TAPPI Sect., 39; C., 1945, 26.

<sup>61</sup> *Ibid.*, 1945, 120, TAPPI Sect., 57; C., 1945, 107.

<sup>62</sup> *Ibid.*, 1944, 119, TAPPI Sect., 221; C., 1945, 107.

<sup>63</sup> *Ibid.*, 1945, 120, TAPPI Sect., 72; C., 1945, 107.



of asphalt presents certain obvious difficulties, and E. G. Mullen<sup>64</sup> suggests overcoming them by placing a watch-glass over the indicator powder, and sealing it and the edges of the square paper sample with a mixture of rosin and beeswax. Under these conditions, a definite relationship exists between the temperature of the water and the penetration rate, so that accelerated tests for routine work may be carried out at 100° F.

A new test for packagings, which has a practical relationship to the war-time uses of V-boards, is the buoyancy test of R. W. K. Ulm.<sup>65</sup> The weighted sample is hung in water from the arm of a balance, which is brought to equilibrium within 15 seconds, and again after 10 minutes. So long as only rosin and/or wax sizing is used, a loss in weight is regarded as indicating sizing satisfactory for V-boards. In this connexion reference should again be made to Barker's work<sup>53</sup> on weatherproof fibre board containing asphalt liners, since this includes testing methods. The TAPPI Cobb test and the "submersion number" (the weight of water absorbed by 6 sq. in. of sample after immersion in water for 10 minutes at 75° F.) are used.

*Optical Methods.*—A further contribution to the measurement of the opacity of paper from the Institute of Paper Chemistry<sup>66</sup> deals with the calibration of the Bausch and Lomb opacimeter, and gives details of a technique for preparing a standard white by depositing a standard thickness of magnesium oxide on a flat-surfaced block of magnesium carbonate. Errors involved when the white backing body is a permanent standard in direct contact with, and separated by a cover glass from, the paper specimen are compared. They are greater in the latter case. H. A. Lips<sup>67</sup> has proposed a method for standardising fading lamps used in light-fastness tests. A suitably dyed piece of paper or cloth (the control) is exposed to the lamp for 20 hours, with the sample, and then matched against one of a series of permanently coloured plastic chips, which illustrate the results of exposure for 12, 14, etc. to 26 hours to a standard lamp. The degree of fading of the sample may thus be related to that produced by a standard lamp; exposures to sunlight may be standardised similarly.

In an improved method for the measurement of fibre dimensions due to J. H. Graff and J. R. Feavel,<sup>68</sup> the stained fibres are projected on to a ground glass screen ( $\times 75$ ) on which the lengths and widths may be measured to within 0.1 and 0.01 mm., respectively. The results are examined statistically, and the distribution of the short, medium, and long fibres is conveniently shown on a triangular chart. Since the densities of fibres from the same source are approximately constant, it is possible to estimate the weights of the fibres from the measured

<sup>64</sup> *Paper Trade J.*, 1944, 119, TAPPI Sect., 11; C., 1945, 171.

<sup>65</sup> *Ibid.*, 87; C., 1945, 26.

<sup>66</sup> *Ibid.*, 1944, 119, No. 17, 27; C., 1945, 26.

<sup>67</sup> *Ibid.*, 1945, 120, TAPPI Sect., 108; C., 1945, 201.

<sup>68</sup> *Ibid.*, 1944, 118, TAPPI Sect., 53; C., 1945, 169.



areas. A new application of ultra-violet light is recorded by W. T. Diefenbach<sup>69</sup>; he uses it to detect irregularities in moisture vapour-proof and other coatings on paper.

Estimations of ink coverage in relation to printability, by three methods, are compared by R. Buchdahl and M. F. Polglase.<sup>70</sup> In the standard gravimetric method the thin copper printing plate used is weighed before and after printing. Alternatively, and preferably, a known, very small quantity of methyl-violet, or of radioactive phosphorus pentachloride, is added to the ink used, and the amounts present in the print are determined colorimetrically (after selective extraction) or by a Geiger-Müller counter, respectively. The new methods must be calibrated against gravimetric determinations.

*Miscellaneous.*—Other revised TAPPI testing methods for paper and board, are: T402 m-41<sup>71</sup> (conditioning, before testing), T410 m-44<sup>72</sup> (basis weight determination), and T461 sm-43<sup>73</sup> (flammability of flame-proofed paper). New TAPPI methods deal with the determination of water-soluble sulphates and chlorides<sup>74</sup> (T468 m-45) by the usual methods, using an extract of the sample in boiling water, and with bacteriological examination<sup>75</sup> (T449 m-45) using the plating-out technique.

<sup>69</sup> *Paper Ind.*, 1944, **26**, 992; C., 1945, 108.

<sup>70</sup> *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 25; B., 1945, II, 311; C., 1946, 22.

<sup>71</sup> *Ibid.*, 1944, **119**, *TAPPI Sect.*, 145; C., 1945, 26.

<sup>72</sup> *Ibid.*, 1945, **120**, *TAPPI Sect.*, 153; C., 1945, 171.

<sup>73</sup> *Ibid.*, 1944, **119**, *TAPPI Sect.*, 39; C., 1945, 171.

<sup>74</sup> *Ibid.*, 1945, **121**, *TAPPI Sect.*, 41; C., 1945, 242.

<sup>75</sup> *Ibid.*, 28; C., 1945, 241.



## ACIDS, ALKALIS, AND SALTS.

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### AMMONIA AND AMMONIUM SALTS.

THERE are no major technical developments to report in the synthetic ammonia field, and according to Allied investigators there was little technical advance in Germany during the war.<sup>1</sup> Following the rapid war-time expansion of synthetic ammonia capacity, notably in the U.S.A., there has been little construction of new plants. However, the long-standing Aswan project in Egypt is again attracting attention,<sup>2</sup> and the Government of India proposes to erect a 350,000 ton per year ammonium sulphate plant in Bihar.<sup>3</sup> Gypsum will be the source of the sulphate radical, and capital and operating cost data of possible schemes are given in the Gowing, Rigg, and Riley Report.<sup>4</sup> The State of Travancore is erecting a plant which is unique in that it will use wood gasification and the steam-iron process for obtaining the necessary hydrogen.<sup>5</sup> Projects are also reported from Spain<sup>6</sup> and Portugal.<sup>7</sup>

On the theoretical side, papers have been published by K. G. Denbigh<sup>8</sup> and G. K. Boreskov and M. G. Slinko<sup>9</sup> on the design of catalysers for exothermic gas reactions, which of course include ammonia synthesis. Both papers give expressions from which the optimum temperature gradient through a converter may be derived. This is the resultant of the two opposing factors, that the approach to equilibrium is more rapid the higher the temperature, and that the equilibrium itself is more favourable the lower the temperature.

In Japan, investigations have been made, apparently on a laboratory scale, on a process for making calcium cyanamide by passing ammonia and carbon dioxide over calcium carbonate heated to 800°<sup>10</sup>; efficiency on ammonia of 93% is claimed. This is an interesting reversal of the older process for making ammonia and it might possibly have application because of the expanding field of chemicals based on dicyanodiamide.

<sup>1</sup> *Chem. Eng. News*, 1945, 23, 1516.

<sup>2</sup> *Oil Col. Tr. J.*, 1945, 108, 603.

<sup>3</sup> *Financial News*, 1944, Nov. 11th, 2.

<sup>4</sup> "Report of Mission to Advise on Production of Artificial Fertilizers in India," Govt. of India Press, 1944.

<sup>5</sup> *Chem. Age*, 1945, 53, 84.

<sup>6</sup> *Foreign Commerce Weekly*, 1944, 16, 622.

<sup>7</sup> *Chem. Age*, 1944, 51, 331.

<sup>8</sup> *Trans. Faraday Soc.*, 1944, 40, 352; A., 1944, I, 287.

<sup>9</sup> *J. Appl. Chem. Russ.*, 1943, 16, 377; B., 1945, I, 49.

<sup>10</sup> *Chem. Trade J.*, 1945, 117, 260.



Most of the published work on ammonium salts has been centred on ammonium sulphate. Several publications<sup>11</sup> from the U.S.A. describe an interesting process for preparing crystalline ammonium sulphate from coke-oven gas. The ammonia is absorbed from the gas in a scrubber tower through which is circulated an acidified ammonium sulphate solution of such a concentration that, after absorption of ammonia, the resulting solution is almost saturated. This solution is then fed to a vacuum concentrator forming part of an Oslo evaporator unit. The supersaturated solution from the vacuum concentrator flows upwards through a bed of crystals in the crystalliser, the supersaturation being relieved by deposition on these crystals. Sulphuric acid is added to the desupersaturated solution from the crystalliser and the solution fed back to the scrubber tower. Thus the rôle of the conventional saturator as both ammonia absorber and crystalliser has in this new process been split into two separate processes. The greater degree of control thus obtained has been utilised to produce a product which is claimed to consist of uniformly large crystals. These crystals are separated and dried on one piece of equipment. The top feed drying salt filter is an interesting modification to the normal top feed salt filter. The complete drum and feeding arrangements are enclosed in a case and the case is fed with heated air at temperatures up to 150° or more. The hot air thus drawn through the cake dries it and produces a product which needs no further drying, moisture content 0.1—0.3%.

Experiments are reported from Germany<sup>12</sup> in which the direct conversion of ammonia and hydrogen sulphide of coke-oven gas into ammonium sulphate was achieved with hydrogen peroxide:  $2\text{NH}_3 + \text{H}_2\text{S} + 4\text{H}_2\text{O}_2 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 + 4\text{H}_2\text{O}$ . Information from the same source contains data on the preparation of ammonium sulphate by scrubbing the gas with a gypsum slurry; 100% conversion of the ammonia was achieved.

T. C. Oliver, R. D. Long, and L. H. Crosson<sup>13</sup> have described the preparation of ammonium sulphate by passing gaseous ammonia into a solution of waste ferrous sulphate, filtering the precipitate, heating it to 140° to make the iron compound stable, and then dissolving out the ammonium salt. Another process,<sup>14</sup> which has been developed for the preparation of ammonium sulphate together with sulphur from exhaust gases containing between 0.15% and 7% by volume of sulphur dioxide, consists in scrubbing the gases with a solution of ammonium sulphite, bisulphite, and sulphate, keeping the pH at a predetermined figure by the addition of aqueous ammonia; the solution is bled off to an autoclave,

<sup>11</sup> *Blast Furn. & Steel Plant*, 1944, 32, 1445; 1945, 33, 976; B., 1945, I, 49. B.P. 569,918; B., 1945, I, 329. U.S.P. 2,383,171. U.S.P. 2,324,222; B., 1946, I, 18.

<sup>12</sup> *Oel u. Kohle*, 1944, 40, 63.

<sup>13</sup> U.S.P. 2,333,672; B., 1946, II, 130.

<sup>14</sup> *Chem. Trade J.*, 1945, 116, 325.



where it is heated with steam to form ammonium sulphate solution and sulphur.

Details of the manufacture of ammonium chloride for industrial purposes by the sulphite process at Hamilton, Ontario, have been published by E. J. R. Cook.<sup>15</sup> The process may be represented by the equation  $2\text{NaCl} + \text{SO}_2 + 2\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_3 + 2\text{NH}_4\text{Cl}$ . Essentially the process consists of mixing equivalent quantities of salt, sulphur dioxide, and anhydrous ammonia in water in a stirred reaction vessel and allowing the reaction to reach equilibrium at 60°; sodium sulphite separates at this temperature. The remaining solution is evaporated at 20°, at which temperature the equilibrium is such that ammonium chloride is precipitated. The cycle is then repeated. The sodium sulphite analyses 96.5%  $\text{Na}_2\text{SO}_3$ , the difference being mainly sodium sulphate, and is used direct in the production of explosives and textiles and also for the production of sodium thiosulphate and metabisulphite. The ammonium chloride analyses 99.85%  $\text{NH}_4\text{Cl}$  on a dry basis and is sufficiently pure to be used in the manufacture of dry batteries.

*Hydroxylamine Salts.*—An interesting method<sup>16</sup> for the preparation of hydroxylamine hydrochloride has been patented by P. J. Ekman and W. O. Walker. Acetone (50 parts) is treated with concentrated hydrochloric acid (75 parts) and concentrated nitric acid (100 parts) for one hour at 30—70° to give chloroacetoxime,  $\text{COMe}\cdot\text{CCl}:\text{N}\cdot\text{OH}$ ; the solution is diluted with an equal volume of water and treated with chlorine at 10—20° to yield phosgeneoxime. This solution may be boiled until the hydrolysis of the phosgeneoxime is complete and then evaporated at reduced pressure until hydroxylamine hydrochloride crystallises out, or the solution may be distilled under reduced pressure to give an aqueous solution of phosgeneoxime which is treated as previously, and leave a residue of chloroacetoxime for re-treatment.

R. M. Joyce<sup>17</sup> describes the pyrolysis of certain nitroparaffins at 200—430° and the separation with an overall yield of 30% of hydroxylamine hydrochloride by passing the reaction products through a condenser into aqueous hydrochloric acid. Better yields of hydroxylamine from nitroparaffins are, however, obtained by hydrolysis, and especially by the hydrolysis of  $\alpha\beta$ -dinitroethane with sulphuric acid and water at 150°, giving an 85% yield of hydroxylamine salt and a 50% yield of oxalic acid.<sup>18</sup>

#### NITRIC ACID AND NITRATES.

Appreciable interest has been shown in the problems of ammonia oxidation and the absorption of nitrous fumes to produce nitric acid.

<sup>15</sup> *Canad. Chem.*, 1945, 29, 221; B., 1945, I, 255.

<sup>16</sup> U.S.P. 2,319,669; B., 1945, I, 255.

<sup>17</sup> U.S.P. 2,307,929; B., 1944, I, 396.

<sup>18</sup> B.P. 573,630; B., 1946, I, 96.



A modified catalyst for ammonia oxidation containing palladium in addition to rhodium in a platinum base has been patented by A. R. Powell<sup>19</sup> with claims for an enhanced life. Two further patents relate to the technique of starting up ammonia oxidation units. N. A. Laury and A. P. Beardsley<sup>20</sup> claim prevention of corrosion by preheating the plant above the dew point of the burner gases before starting up, and R. S. Richardson<sup>21</sup> claims a method of heating the plant by interchange of heat between products of combustion and air.

M. J. Kalous has patented two methods of producing mist during the absorption of nitrous gases in order to increase the surface available for reaction. The first method<sup>22</sup> consists of the addition of steam to the gases and the second<sup>23</sup> of varying the temperature in successive stages of absorption over a range of about 40° minimum. In both cases the process is to be applied only where the concentration of the absorbing acid is less than 40%. The kinetics of the oxidation of nitric oxide to the dioxide has been studied by A. M. Murzin,<sup>24</sup> who predicts minimum reaction time at 6.9% and 10.4% oxygen when the ratio of oxygen to nitric oxide is greater than 10. The use of superheated steam in place of air for acid lifts in nitric acid concentration plant has been patented by F. C. Zeisberg.<sup>25</sup>

An interesting series of reactions involving the use of chlorine in the presence of nitrous gases and oxygen is brought forward again by the renewal of certain patents by the Solvay Process Co.:  $6\text{NO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HNO}_3 + 2\text{NOCl}$ ;  $2\text{NOCl} + \text{O}_2 = 2\text{NO}_2 + \text{Cl}_2$ ;  $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$ . One of the patents<sup>26</sup> relates to the drying of gases containing nitrosyl chloride by washing with liquid nitrosyl chloride with or without chlorine, and another<sup>27</sup> relates to the use of the above reactions to produce concentrated nitric acid from 70% nitric acid and nitrous gases containing chlorine; the final concentrated acid contains more than 0.5% of hydrogen chloride. A further use of these reactions has been patented by the Solvay Process Co.<sup>28</sup> for the manufacture of sodium nitrate from sodium chloride. The reaction mixture is kept boiling and the liberated gases are scrubbed by the incoming weak nitric acid, which is thereby concentrated from about 30% to 45%. The products are chlorine, nitrogen tetroxide, and an acid solution of sodium nitrate with chloride impurity.

The possibility of using ammonium nitrate as a fertiliser is a matter which is receiving considerable attention. Many of the practical aspects

<sup>19</sup> B.P. 570,071; B., 1945, I, 329.

<sup>20</sup> U.S.P. 2,192,816; B., 1945, I, 292.

<sup>21</sup> U.S.P. 2,185,607; B., 1945, I, 22.

<sup>22</sup> B.P. 565,728; B., 1945, I, 64.

<sup>23</sup> B.P. 569,687; B., 1945, I, 293.

<sup>24</sup> *J. Appl. Chem. Russ.*, 1944, 17, 307; B., 1945, I, 328.

<sup>25</sup> U.S.P. 2,190,304; B., 1945, I, 328.

<sup>26</sup> U.S.P. 2,320,257; B., 1945, I, 185.

<sup>27</sup> U.S.P. 2,185,579; B., 1945, I, 21.

<sup>28</sup> U.S.P. 2,181,559; B., 1945, I, 22.



of such uses are covered by W. H. Ross, J. R. Adams, J. Y. Yee, and C. W. Whittaker,<sup>29</sup> who point out that temperature variations and moisture are the major cause of caking. Caking can be minimised by granulation and by coating with substances such as kaolin or kieselguhr. The addition of water-repellent binders such as resin, petrolatum, etc. is advantageous. None of these coatings overcomes the hygroscopic nature of ammonium nitrate but the material stores well in moistureproof containers and drills well. A size range of 8—16-mesh is said to be best for drilling.

The use of the non-hygroscopic nitrates of calcium, strontium, barium, magnesium, or zinc as dusting agents to prevent the caking of sodium and potassium nitrites has been patented by F. S. Chambers.<sup>30</sup> The formation of a complex between sodium nitrite and sulphur trioxide has been patented by S. Z. Avedikian<sup>31</sup>; on reaction with water nitrous fumes are evolved and the material is suggested as a convenient source of small amounts of nitrous fume for bleaching.

#### PHOSPHATES.

A world review of the phosphate rock industry, including production statistics, mining, purification, and grinding, has been published.<sup>32,33</sup> The output of phosphate rock in French Morocco declined after the first quarter of the year and it is doubtful if the projected output of 2,600,000 tons will be achieved. Shortage of electric power, coal, labour, and equipment is responsible for the decline in output but difficulty is also being experienced in drying the rock and transporting it to port.<sup>32</sup> Most of the U.K. demands for phosphorus were nevertheless met by the importation of North African phosphate rock although some phosphorus and granular ammonium dihydrogen phosphate have come from North America.

The production and sales of phosphate rock in the United States of America during 1944 each exceeded 5,000,000 tons and were the highest yet achieved, but it is expected that some decline in demand will follow the cessation of hostilities.<sup>34</sup> Most of the rock was used in the manufacture of superphosphate and it is of interest that less than 5% of the fertiliser made was in the form of triple superphosphate.<sup>35</sup> The re-occupation of Nauru Island by the Allied forces has not yet improved the supply position in Australia and New Zealand owing to the destruction of equipment on the island. New machinery is being sent but shipments

<sup>29</sup> *Ind. Eng. Chem.*, 1944, **36**, 1088; *B.*, 1945, **I**, 124.

<sup>30</sup> U.S.P. 2,316,154; *B.*, 1945, **I**, 221.

<sup>31</sup> U.S.P. 2,320,058; *B.*, 1945, **I**, 221.

<sup>32</sup> *Chem. Met. Eng.*, 1945, **52**, No. 11, 188.

<sup>33</sup> *Min. & Met.*, 1944, **25**, 454; *Rock Prod.*, 1944, **47**, Nov., Dec.; 1945, **48**, Jan., Feb., April; *Eng. Min. J.*, **146**, 81, 1945.

<sup>34</sup> *Fert. Feeding Stuffs J.*, 1945, **31**, 475.

<sup>35</sup> *Chem. Met. Eng.*, 1945, **52**, No. 2, 135.



of phosphate rock in 1946 are not expected to be considerable.<sup>36</sup> The Soviet Government has now released the information that huge deposits of phosphate rock have been opened up in Khazakhstan, Central Asia. The reserves so far established are more than 1000 million tons and the deposit exceeds in importance the apatite found in the Kola Peninsula. Plans are in an advanced state for the establishment of a comprehensive chemical industry to exploit this Khazakhstan phosphorite.<sup>37</sup>

Comparatively little work has been published during the year on methods of making the  $P_2O_5$  of phosphate rock available as a plant food by wet acid processes. The I.G. Farbenindustrie claim that the filterability of gypsum produced by interaction of phosphate rock and sulphuric acid is improved if aluminium and fluorine compounds are added to give minimum aluminium oxide and fluorine concentrations of 0.3% and 0.1% respectively during the crystallisation of the gypsum.<sup>38</sup> The T.V.A. (G. L. Bridger, R. B. Burt, and W. W. Cerf) has reviewed its experience in the manufacture of triple superphosphate.<sup>39</sup> The phosphoric acid used to react with the phosphate rock contains 78% of orthophosphoric acid and laboratory experiments indicate that conversion in the plant could be improved considerably by lowering the reactant and curing temperatures and by improving the thoroughness of mixing. A decrease in reactant temperature has a beneficial effect on conversion only if the acid contains more than 70% of phosphoric acid; at lower concentrations, a decrease in the reactant temperature usually reduces the conversion. Maximum conversion is obtained with acid containing 70% of phosphoric acid, but the difficulty of handling and the longer curing time required for the resultant triple superphosphate make it more practicable to achieve improved conversion by using 78% acid and cooling the reactants than by using 70% acid. Owing to wartime conditions the laboratory results have not yet been applied to plant operation.

Research on the treatment of phosphate rock at high temperatures has continued. The process in which the apatite structure of phosphate rock is disrupted by fusing a mixture of rock and silica in a vertical shaft furnace in the presence of water vapour has been further studied by K. L. Elmore.<sup>40</sup> It is claimed that the fluidity of the melt is increased and the rate of fluorine removal is enhanced by adjusting the composition of the furnace charge so that for each molecule of calcium oxide in excess of that present as  $Ca_3(PO_4)_2$ , the charge contains 2 mols. of silica and 1 mol. of either silica, ferrous oxide, ferric oxide, or aluminium oxide or a mixture of these oxides. The melting point of such a mixture is about  $1460^\circ$  and material made at  $1485^\circ$  was free from fluorine and contained 61.2% of  $Ca_3(PO_4)_2$  in which 88.3% of the  $P_2O_5$  was available as a plant

<sup>36</sup> *Fert. Feeding Stuffs J.*, 1945, 31, 733.

<sup>37</sup> *Chem. Trade J.*, 1945, 117, 128.

<sup>38</sup> Belg.P. 443,916.

<sup>39</sup> *Ind. Eng. Chem.*, 1945, 37, 829; B., 1946, I, 16.

<sup>40</sup> U.S.P. 2,368,649.



food. The effectiveness of fused defluorinated phosphate rock as a fertiliser depends according to G. L. Terman on the particle size, which must be below 60-mesh.<sup>41</sup>

The reduction of phosphate rock with coke in a blast or electric furnace yields phosphorus and carbon monoxide as gaseous products. G. L. Frear, E. F. Ogg, and L. H. Hull of the T.V.A. have shown that all the phosphorus in blast- or electric-furnace gases can be oxidised to phosphorus pentoxide at 400—600°. The rate of oxidation of carbon monoxide is very slow in this temperature range so that the carbon monoxide is almost unaffected and can subsequently be used as a fuel gas. An excess of 20—40% of oxygen as air should be added to electric-furnace gas and 50—100% excess to blast-furnace gas. Alternatively, the blast-furnace gas can be made to react with phosphate rock at 950—1100° to give complete oxidation of the phosphorus (removed as calcium metaphosphate) but 10—25% of the carbon monoxide is simultaneously oxidised.<sup>42</sup>

German patents dealing with modifications to the Rhenania process have been filed.<sup>43</sup> A claim has also been made that a citrate-soluble alkali fertiliser is obtained by sintering phosphate rock and an alkali phosphate under reducing conditions.<sup>44</sup> The Ministry of Supply announced the production of silico-phosphate early in the year but supplies did not reach the market until the year end, suggesting that manufacturing difficulties had been encountered. Silico-phosphate is made by calcining a mixture of phosphate rock, sand, and soda ash in a rotary cement kiln and contains 30—33% of  $P_2O_5$  of which 80—85% is citrate-soluble.

Bonemeal has been in short supply in the U.S.A. during the war and search has been made for a satisfactory substitute for use as a phosphorus supplement in animal feeding stuffs. H. R. Bird, J. P. Mattingly, H. W. Titus, J. C. Hammond, W. L. Kellogg, T. B. Clark, C. E. Weakley, jun., and A. H. Van Landingham report that phosphate rock itself is unsuitable owing to its high fluorine content but defluorinated phosphate rock has been found to be almost as completely assimilated by the animal as bonemeal.<sup>45</sup> It is reported by N. R. Ellis, C. A. Cabell, W. P. Elmslie, G. S. Fraps, P. H. Phillips, and D. E. Williams that superphosphate calcined at a high temperature loses most of its fluorine but the product is less satisfactory as a phosphorus supplement than defluorinated phosphate rock.<sup>46</sup> A laboratory study<sup>47</sup> by E. J. Fox, D. S. Reynolds, K. D. Jacob, and W. L. Hill of the thermal defluorination of superphosphate showed that 80%

<sup>41</sup> *Proc. Soil Sci. Soc. Amer.*, 1944, 9; 1945, 154.

<sup>42</sup> *Ind. Eng. Chem.*, 1945, 36, 927; B., 1945, I, 98. U.S.P. 2,374,188.

<sup>43</sup> G.P. 744,998, 744,999, and 740,412.

<sup>44</sup> G.P. 740,413.

<sup>45</sup> *J. Assoc. Off. Agric. Chem.*, 1945, 28, 118; A., 1945, III, 456.

<sup>46</sup> *Ibid.*, 129; A., 1945, III, 456.

<sup>47</sup> *Abstracts of Papers, 108th Meeting, A.C.S.*, 12F.



of the fluorine was volatilised in 15 minutes at  $500^{\circ}$  and 97—99% at  $700$ — $1000^{\circ}$ . In the temperature range  $500$ — $800^{\circ}$  less than 50% of the  $P_2O_5$  in the calcined product was soluble in 0.4% hydrochloric acid, compared with 95% in the original superphosphate, but at  $1000^{\circ}$  the solubility had risen to 85%. Reaction between calcium phosphate and calcium sulphate, with volatilisation of sulphur compounds, began at  $600^{\circ}$  and increased progressively with temperature. The principal constituents in superphosphate calcined at  $500$ — $600^{\circ}$ ,  $650$ — $750^{\circ}$ , and  $1000$ — $1100^{\circ}$  are  $\beta$ - $Ca(PO_3)_2$ ,  $\beta$ - $Ca_2P_2O_7$ , and  $\beta$ - $Ca_3(PO_4)_2$  respectively. The difficulties normally encountered in the calcination of superphosphate caused by fusion and evolution of sulphur compounds are said by C. A. Butt<sup>48</sup> to be overcome by mixing the superphosphate before calcination with a basic alkaline-earth compound in excess of that required to neutralise the free acid.

Industrial precipitated tricalcium phosphates have been found by W. H. McIntire, S. H. Winterberg, H. L. Marshall, G. Palmer, and B. W. Hatcher<sup>49</sup> to vary widely in composition and solubility in ammonium citrate. A process has been described by W. H. McIntire, G. Palmer, and H. L. Marshall,<sup>50</sup> consisting of the slow addition of concentrated phosphoric acid to a cooled concentrated sucrose solution saturated with lime, for the production of tricalcium phosphate as a "reference" material for chemical, fertiliser, and biochemical research. Tricalcium phosphate can be differentiated from hydroxyapatite by the greater solubility of its calcination product in ammonium citrate. These studies are of interest in connexion with the reactions that occur during the ammoniation of superphosphate. W. H. McIntire, H. L. Marshall, and R. C. Shank<sup>51</sup> have investigated the effect of the proportions of the reactants, temperature, added calcium sulphate, ageing, component fluorides, and method of citrate digestion as factors in establishing the transitions induced by gaseous and aqueous ammoniation of superphosphate. The results confirm that hydroxyapatite reacts much more readily than tricalcium phosphate with fluorides and that the development of hydroxyapatite during the ammoniation of superphosphate thus facilitates the formation of apatite. This is in agreement with earlier work which showed the necessity for carefully limiting the quantity of ammonia in the ammoniation of standard superphosphate. Triple superphosphate, however, can with adequate temperature control be highly ammoniated without seriously increasing the content of citrate-insoluble material.

L. E. Berlin and S. I. Volfkovitsch have studied the decomposition of natural borates by phosphoric acid to yield boric acid and fertilisers.<sup>52</sup>

<sup>48</sup> U.S.P. 2,360,197.

<sup>49</sup> *Ind. Eng. Chem.*, 1944, **36**, 547; B., 1944, I, 363.

<sup>50</sup> *Ibid.*, 1945, **37**, 164; A., 1945, I, 173.

<sup>51</sup> *J. Assoc. Off. Agric. Chem.*, 1944, **27**, 413; B., 1945, I, 97.

<sup>52</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1944, 172; B., 1945, I, 125.



A boron-containing fertiliser can be made by treating ascarite (25.2%  $B_2O_3$ ) with phosphoric acid, causing separation of boric acid, and subsequent neutralisation with ammonia to give material containing  $P_2O_5$  52.7,  $NH_3$  10.9, and  $B_2O_3$  4.7%. The use of calcium carbonate for neutralisation yielded a product with  $P_2O_5$  39.3 and  $B_2O_3$  3.1%. Phosphoric acid may also be used for the decomposition of argillaceous hydroborates of low (6.6%)  $B_2O_3$  content, giving a fertiliser having  $P_2O_5$  21.9—27.8,  $SO_3$  30.3—25.3,  $CaO$  23.0—20.3,  $MgO$  3.6—4.4, and  $B_2O_3$  2.7—3.3%. The fertilisers are non-hygroscopic in air of less than 75% humidity.

Very little has been reported on the preparation of phosphate salts for industrial purposes. A. H. Fiske prepares granular non-friable monocalcium phosphate for baking powders by adding an acid-soluble phosphate of iron, aluminium, or chromium to 76% phosphoric acid before neutralising it with lime. The product contains about 1.25% of tervalent metal phosphate.<sup>53</sup> Another method by L. Block and C. S. King for making granular free-flowing monocalcium phosphate is by heating dicalcium phosphate, phosphoric acid, water, and acetone under reflux at 55°.<sup>54</sup>

#### SULPHUR AND SULPHURIC ACID.

*Sulphur.*—A process for manufacture of elemental sulphur from ores and gases containing sulphur has been patented by G. Gaither.<sup>55</sup> Sulphur dioxide generated by burning pyrites is divided into two portions. One passes through an absorption system containing sodium carbonate, whereby aqueous sodium bisulphite is formed, and the liberated carbon dioxide is brought in contact with aqueous sodium sulphide: the hydrogen sulphide so generated is allowed to react with the other portion of sulphur dioxide to form sulphur. The sodium carbonate from the hydrogen sulphide generation is returned to the first absorption stage and the sodium bisulphite, after treatment with sodium carbonate to convert it into sodium sulphite, is evaporated to dryness and the residue reduced to sodium sulphide by fusion with carbon.

*Sulphur dioxide and Sulphuric Acid.*—Several processes are described for production of sulphur dioxide. P. P. Budnikov and I. I. Rivlin<sup>56</sup> state that the optimum conditions for obtaining sulphur from slag are to heat 92 parts of the slag at 1460—1480° in an air current with 8 parts of a mixture of gypsum and dolomite; 80% of sulphur can be recovered as sulphur dioxide and the residue is suitable for use as a cement base.

For the sulphite wood-pulping process, R. B. Murchie<sup>57</sup> claims that replacement of rotary burners by spray burners has resulted in the considerable advantages of simpler operation, speedier starting up,

<sup>53</sup> U.S.P. 2,182,613; B., 1945, I, 62.

<sup>54</sup> U.S.P. 2,181,933; B., 1945, I, 62.

<sup>55</sup> U.S.P. 2,177,707; B., 1944, I, 365.

<sup>56</sup> J. Appl. Chem. Russ., 1943, 16, 11; B., 1945, I, 61.

<sup>57</sup> Pulp & Paper Mag. Canada, 1944, 45, 957; B., 1945, I, 125.



higher sulphur dioxide concentration, and lower sulphur trioxide. He also claims that the formation of insoluble calcium oxide deposits in the digesters is almost completely eliminated and that the loss of the sulphur fed to the burner is reduced to almost half.

W. H. Swanson, L. Lang, and D. C. Porter (Assrs. to Paper Patents Co.),<sup>58</sup> considering sulphur dioxide production for the same purpose, describe a process in which sulphur is burned with an approximately theoretical proportion of air at 980—1320°. The gas containing sulphur dioxide is cooled to approximately 230° in a steam-raising boiler and then passed up a cooling tower countercurrent to a water spray followed by an absorption tower where approximately 33% of the sulphur dioxide is absorbed in water. The sulphur dioxide is stripped from this solution by heat exchange or a stream of residual inert gas and the remainder of the sulphur dioxide is absorbed in milk of lime.

Processes for recovery of dilute sulphur dioxide have been described by American Smelting & Refining Co.<sup>59</sup>; the sulphur dioxide is absorbed in an aromatic amine, for example dimethylaniline, from which it can be recovered. L. J. B. Guyard<sup>60</sup> in a similar process uses a solution of beryllium sulphate containing excess of beryllia. A litre of the solution containing 435 g. of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and 109 g. of  $\text{BeO}$  is capable of dissolving 186 g. of sulphur dioxide and the sulphur dioxide can be regenerated by boiling under reduced pressure.

There is little to report on either the contact process or the chamber process. E. I. Du Pont de Nemours & Co.<sup>61</sup> describe a method of production of acid in which cold moist burner gases are scrubbed with sulphuric acid of drying acid concentration containing lead so as to dilute the acid and precipitate lead sulphate, which is removed; the treated dilute acid is then used to absorb sulphur trioxide made from dry and converted burner gas.

The efficiency of absorption of sulphur trioxide by 75—95% aqueous sulphuric acid has been studied by A. G. Amelin.<sup>62</sup> It decreases with decreasing acid concentration and with rising temperatures between 20° and 105°. At higher temperatures it increases with rising temperatures and is independent of the admixture of steam. The temperature for complete absorption corresponds with the over-saturation, limits being 173°, 183°, and 193° respectively for acid concentrations of 95, 90, and 85%.

A method of preparing 20% sulphuric acid is claimed by J. H. Walthall.<sup>63</sup> By interaction of a gas mixture containing 15—16% of sulphur dioxide and 17—18% of oxygen with a solution containing

<sup>58</sup> U.S.P. 2,188,321; B., 1945, I, 153.

<sup>59</sup> B.P. 564,734; B., 1945, I, 24.

<sup>60</sup> U.S.P. 2,314,936; B., 1945, I, 185.

<sup>61</sup> B.P. 565,737; B., 1945, I, 62.

<sup>62</sup> *J. Appl. Chem. Russ.*, 1944, 17, 319; B., 1945, I, 327.

<sup>63</sup> U.S.P. 2,188,324; B., 1945, I, 153.



about 0.05% of manganese and 0.16% of aluminium as sulphates, about 40% of the sulphur dioxide is absorbed.

A process for treatment of sulphuric acid for removal of nitrogen oxides is claimed by N. C. Somers and W. C. Woodings, jun. (Assrs. to E. I. Du Pont de Nemours & Co.),<sup>64</sup> who add 3 parts of saturated aqueous ferrous sulphate to 100 parts of 97% sulphuric acid containing 0.19% of sulphur dioxide and 0.014% of nitric oxide and then aërate at 38° with air. Nitric oxide is removed completely and less than 0.0001% of sulphur dioxide remains.

According to F. M. Archibald (Assr. to Standard Oil Development Co.)<sup>65</sup> sulphuric acid from petroleum refinery reactions can be purified and freed from 0.5—1% of carbonaceous material by precipitating by dilution, concentrating to 88—90%, and then circulating through a tower at 175—225°, where it is allowed to react with 1.5—3% by weight of concentrated nitric acid; it is then purified from nitrogen oxide compounds by treatment with ammonia in a second tower. The nitrogen compounds are recovered by absorption from both towers. The acid so treated yields no precipitate on dilution. V. R. Kokatnur and J. J. Jacobs, jun. (Assrs. to Autoxygen Inc.),<sup>66</sup> treat sulphuric acid sludge from petroleum distillates by passing it countercurrent through vapours of a water-immiscible organic solvent.

According to J. V. Shinn (Assr. to General Chemical Co.),<sup>67</sup> impure sulphuric acid containing organic froth-promoting agents can be concentrated in the normal way until frothing begins, when a saturated fatty acid, or its ester or salt, is added to reduce frothing and cause deposited calcium to form as discrete particles, which are readily separated.

An interesting information manual has been issued by the Royal Ordnance Factories (Explosives)<sup>68</sup> dealing with materials of construction and design of storage vessels, pipe lines, valves, pumps, eggs, and air lifts for sulphuric acid, nitric acid, and their mixtures. Stoneware is not mechanically satisfactory except for small containers, but mild steel is generally satisfactory for concentrations greater than 70% sulphuric acid, though corrosion becomes serious, particularly in pipe bends at 50—60°. Silicon-iron is highly resistant to sulphuric acid at all concentrations but is mechanically too similar to ceramic material for general use; it should contain 14.2% of silicon. Lead is satisfactory for sulphuric acid, especially dilute acid, and should contain less than 0.005% of bismuth, and where subject to alternating thermal or mechanical stress, 0.06% of copper; regulus metal is recommended for impellers etc.,

<sup>64</sup> U.S.P. 2,315,988; B., 1945, I, 183.

<sup>65</sup> U.S.P. 2,313,910; B., 1945, I, 221.

<sup>66</sup> U.S.P. 2,320,242; B., 1945, I, 221.

<sup>67</sup> U.S.P. 2,313,677; B., 1945, I, 21.

<sup>68</sup> *Ind. Chem.*, 1944, 20, 345, 416, 475, 537; B., 1944, I, 394.



where increased hardness is desirable. Consideration is also given to storage, transport, jointing, valves, and so on, together with safety precautions at the design stage and during operations.

A process for production of ferric sulphate is described by T. V. Fowler and H. F. Merriam (Assrs. to General Chemical Co.),<sup>69</sup> who state that ferrous sulphate from spent pickle liquor can be converted into anhydrous ferric sulphate by heating it with sulphuric acid in a rotary kiln at 274—450°.

R. P. Smith and J. Belding (Assrs. to Chemical Construction Corporation)<sup>70</sup> recover waste ferrous sulphate from pickle liquor by treating it with sufficient sulphuric acid to restore the original acid content and sufficient ferrous sulphate to maintain a saturated solution in the subsequent filtration stage. The solution is evaporated and filtered at 90—100° to separate ferrous sulphate monohydrate equivalent to the acid added. The mother-liquid is evaporated to yield the heptahydrate and a solution suitable for re-use as a pickling solution. The monohydrate can be calcined to recover sulphuric acid.

K. A. Kobe and W. Dickey<sup>71</sup> have studied the oxidation of ferrous sulphate with air up to 100—170° and 3—275 lb. per sq. in. oxygen partial pressure in the presence of copper sulphate and sulphuric acid. The optimum copper sulphate concentration is 0.1 mol. and the rate of oxidation increases with temperature and pressure, and decreases with increasing sulphuric acid concentration. Mercury and acetaldehyde inhibit the oxidation, but manganese does not affect it.

### HALOGENS.

A number of interesting papers have appeared in which the history of the development of alkali-chlorine cells has been recorded and some notable additions made to the published knowledge concerning their operation. R. B. McMullin and W. C. Gardiner<sup>72</sup> give an account of the electrochemical and allied industries established in the neighbourhood of Niagara. They deal with alkali-chlorine factories, electrothermic works for making abrasives, calcium carbide, ferro-alloys, and graphite, and a number of other concerns using power for metal winning, electro-smelting, electro-melting, and fixation of nitrogen.

L. D. Vorce<sup>73</sup> deals with the development of alkali-chlorine cells in America. His paper is mainly concerned with the history of the diaphragm cell, which is the basis of the bulk of the American chlorine industry and to which American industrial scientists, including this author, have contributed greatly.

<sup>69</sup> U.S.P. 2,184,419; B., 1945, I, 99.

<sup>70</sup> U.S.P. 2,185,095; B., 1945, I, 23.

<sup>71</sup> *Ind. Eng. Chem.*, 1945, 37, 429; B., 1945, I, 328.

<sup>72</sup> *Trans. Electrochem. Soc.*, 1944, 86, *Preprint* 19, 217; B., 1945, I, 61.

<sup>73</sup> *Ibid.*, *Preprint* 3, 29; B., 1944, I, 395.



R. L. Murray and M. S. Kircher<sup>74</sup> are responsible for a detailed study of the current efficiency losses of the Hooker type-S chlorine diaphragm cell. They list the reactions at the anode and cathode which are considered to involve loss of efficiency and show, incidentally, that current efficiency can be approximately estimated for control purposes by the determination of the anolyte pH and also by measuring the oxygen and carbon dioxide content of the cell gas, the latter method being the more generally accurate. Loss of yield of caustic soda is due almost wholly to migration of hydroxyl ions through the diaphragm from catholyte to anolyte.

L. P. Wenzell, P. J. Stuber, and S. Cottrell<sup>75</sup> discuss cylindrical chlorine cells, dealing less with mechanisms than with factory data concerning caustic concentration and voltage as a function of diaphragm life, and current efficiency as a function of the caustic concentration. They point out that reliable data can be obtained only by statistical analysis of tests on a large number of cells. Emphasis is placed on the desirability of reducing the frequency of diaphragm changes and of improving the life of the graphite anodes.

N. J. Johnson<sup>76</sup> describes a laboratory alkali-chlorine cell duplicating as closely as possible the anodic conditions in commercial cells and set up for the purpose of determining the influence on graphite anode corrosion of brine concentration, anode current density, and cell temperature. Anode current density had little effect on weight of anode loss per 1000 amp.-hours (per unit weight of chlorine made) but increasing brine concentration and decreasing temperature very markedly reduced it.

Two processes for production of chlorine by electrolysis are those of W. C. Gardiner (Assr. to Mathieson Alkali Works)<sup>77</sup> by electrolysis of molten magnesium chloride and by D. J. Kennedy and W. E. Barker (Assrs. to Shawinigan Chemicals, Ltd.)<sup>78</sup> by electrolysis of chromium chloride. In the Mathieson process molten magnesium chloride is electrolysed in a cell having a number of anodes. The bath is replenished by addition of hydrated magnesium chloride at some, but not all, of the anodes in presence of the anodic chlorine. The gases evolved during additions are drawn off separately, thus rendering possible the recovery of most of the generated chlorine. In the chromium chloride cells, provision is made for independent circulation of both electrolytes without mixing and without exposure to atmosphere. The electrodes are co-axial tubes with the anode inside and the tubular diaphragm is placed between them; they are arranged in parallel pairs with one connecting chamber of anolyte at the bottom, and three chambers at the top built up of flat graphite plates.

<sup>74</sup> *Trans. Electrochem Soc.*, 1944, 86, *Preprint* 2, 7; B., 1944, I, 396.

<sup>75</sup> *Ibid.*, *Preprint* 13, 169; B., 1945, I, 61.

<sup>76</sup> *Ibid.*, *Preprint* 9, 111; B., 1945, I, 61.

<sup>77</sup> B.P. 570,174; B., 1945, I, 330.

<sup>78</sup> U.S.P. 2,324,002; B., 1945, I, 223.



There is again considerable interest in the production of chlorine from hydrochloric acid. F. W. de Jahn (Assr. to A. N. Mann)<sup>79</sup> has described the oxidation of hydrochloric acid with oxygen at 385—435° in the presence of catalyst containing oxides of various metals such as copper and vanadium followed by scrubbing with sulphuric acid to remove water. F. R. Balcar (Assr. to Air Reduction Co.)<sup>80</sup> describes a similar process, also with a copper and rare-earth compound catalyst, but he washes the effluent gases with aqueous hydrochloric acid to remove unused hydrochloric acid and the solution so obtained is used to purify the incoming hydrochloric acid and reduce catalyst poisoning.

A. Lippman, jun.,<sup>81</sup> draws attention to the use of "Karbate," a graphitic material, for use with hydrochloric acid, stating that it is much cheaper than tantalum and glass, less liable to crack than glass, and has a very much higher overall heat-exchange coefficient.

There are again several patents connected with the production of chlorine dioxide, particularly for generation of chlorine dioxide from chlorine and sodium chlorite. Industrial equipment for the generation of chlorine dioxide is described by E. R. Woodward,<sup>82</sup> who treats moist solid sodium chlorite with chlorine diluted with air; the partial pressure of the chlorine dioxide in the resulting mixture is kept below 30 mm. to reduce explosion dangers. It is claimed that, in addition to its bleaching action, the use of chlorine dioxide on flours improves dough handling and that it can be used for bleaching starch, soap, paper, and textiles and preserving vegetables.

#### SODIUM COMPOUNDS.

Salt has many uses and provides the main source of sodium compounds, and attempts to extend the supplies of salt have included a discussion by I. G. Drushinin<sup>83</sup> of the possibility of obtaining salt from some lakes in Western Siberia, and a summary by A. Gonzalez Zuniga<sup>84</sup> of the principal Peruvian salt deposits. S. S. Aiyar<sup>85</sup> describes how, in making salt by evaporation of Sambhar Lake in India, the residual bitterns contain sulphate, carbonate, bicarbonate, and small amounts of sulphide and silicate, but are free from the magnesium and potassium compounds usually found in bitterns. Salt readily cakes during storage, and the various ways of treating it to avoid caking include the addition of about 0.05% of 50% aqueous sorbitol, as suggested by M. Segura, Assr. to Jefferson Island Salt Mining Co.<sup>86</sup> V. I. Nikolaev and T. I. Arnold<sup>87</sup>

<sup>79</sup> U.S.P. 2,191,980-1; B., 1945, I, 222.

<sup>80</sup> U.S.P. 2,312,952; B., 1945, I, 185.

<sup>81</sup> *Chem. Met. Eng.*, 1945, 52, No. 3, 112; B., 1945, I, 254.

<sup>82</sup> *Chem. Eng. News*, 1944, 22, 1092; B., 1945, I, 21.

<sup>83</sup> *J. Appl. Chem. Russ.*, 1943, 16, 308; B., 1945, I, 61.

<sup>84</sup> *Bol. Soc. Quim. Peru*, 1944, 10, 23; B., 1944, I, 363.

<sup>85</sup> *J. Sci. Ind. Res. India*, 1944, 3, 198; B., 1945, I, 125.

<sup>86</sup> U.S.P. 2,183,173; B., 1945, I, 99.

<sup>87</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1942, 231; B., 1945, I, 152.



describe how double recrystallisation as  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  from distilled water can be used to give salt of 99.99% purity.

A variation in the method of working the ammonia-soda process has been described by C. N. and R. E. Windecker<sup>88</sup> which avoids the need for operating limekilns to give good quality carbon dioxide and avoids some of the compression, by carrying out the first part of the carbonation in the gas phase. Thus, the ammonia is made to react with a kiln gas and cooled, and the mixture of solids is added to brine and bicarbonated to give sodium bicarbonate, using concentrated carbon dioxide obtained by decomposition of the bicarbonate. Similar methods have been proposed before, but in practice they merely provide an unnecessary complication.

J. C. Garrels and H. Roderick (Assrs. to Michigan Alkali Co.)<sup>89</sup> propose to make pure caustic soda by converting calcium chloride solution and ammonium carbonate into pure calcium carbonate, which is calcined and used to causticise pure sodium carbonate; this seems an expensive way of removing the impurities from limestone. H. vom Hove<sup>90</sup> describes a process for obtaining electrolytic caustic soda from waste sodium sulphate solution from viscose manufacture using cellulose diaphragms. According to H. H. Heller<sup>91</sup> the colour of electrolytic caustic liquor is considered to be due to pyromellitic acid chloroquinone, probably an oxidation product of the graphite anodes, and a method of purification suggested by I. E. Muskat and W. F. Waldeck (Assrs. to Pittsburgh Plate Glass Co.)<sup>92</sup> involves crystallising  $\text{NaOH} \cdot 2\text{H}_2\text{O}$  by cooling 57% liquor below 28°.

S. Z. Makarov and L. S. Itkina<sup>93</sup> have confirmed the known method of using sodium sulphate and sodium carbonate for removing chloride from caustic soda and shown that the precipitate can be obtained in a crystalline filterable form. M. J. Kermer<sup>94</sup> describes a method for removing salt from electrolytic caustic liquor during the evaporation process, and I. E. Muskat (Assr. to Pittsburgh Plate Glass Co.)<sup>95</sup> has patented a method for avoiding metallic contamination during evaporation by using evaporator tubes constructed of or lined with carbon. The practice of transporting caustic soda as 50% or 75% liquor is increasing, and C. W. Rippie and A. H. Copeland<sup>96</sup> describe safe methods of handling such liquors which involve storage at above 55° F. and 150° F. respectively in welded steel tanks, the use of cast iron pumps, and covering of pipe joints to prevent squirting. One use of caustic soda is for scrubbing

<sup>88</sup> U.S.P. 2,189,826; B., 1945, I, 328.

<sup>89</sup> U.S.P. 2,180,755; B., 1944, I, 364.

<sup>90</sup> *Chem. Technik*, 1942, 15, 19; B., 1945, I, 182.

<sup>91</sup> *Trans. Electrochem. Soc.*, 1945, 87, *Preprint* 9, 95; B., 1945, I, 182.

<sup>92</sup> U.S.P. 2,178,694; B., 1944, I, 396.

<sup>93</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1944, 283; B., 1945, I, 291.

<sup>94</sup> *Trans. Electrochem. Soc.*, 1944, 86, *Preprint* 24, 265; B., 1945, I, 96.

<sup>95</sup> U.S.P. 2,309,412; B., 1945, I, 99.

<sup>96</sup> *Chem. Eng. News*, 1944, 22, 1164; B., 1944, I, 363.



gases to remove carbon dioxide, and calculations by T. P. Dee<sup>97</sup> show that the partial pressure of carbon dioxide over such solutions at 20° is only about  $10^{-11}$  atmosphere even when 90% of the caustic has been converted into carbonate.

Sodium compounds are also obtained as carbonate and sulphate from natural lakes. A study by G. S. Sedelnikov<sup>98</sup> of the system  $\text{Na}_2\text{CO}_3\text{--Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  has been made at 100° with the object of extracting sodium carbonate from natural waters. The solid phases at this temperature are sodium carbonate monohydrate, a sulphate-carbonate mixed crystal, sodium sulphate, and sodium chloride. The sulphate-carbonate complex can be resolved into  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$  by crystallisation at 22°, leaving a liquor rich in carbonate which can be recovered. Thin tanks with flat distortable walls provide an easy means, patented by T. F. Banigan and O. E. Snyder (Assrs. to E. I. Du Pont de Nemours & Co.),<sup>99</sup> of crystallising Glauber's salt by refrigeration. According to D. J. Pye (Assr. to Dow Chemical Co.),<sup>100</sup> sodium sulphate and sodium chloride crystals can be separated by froth flotation in an alkaline brine containing caustic soda, using a fatty acid in presence of a material yielding any of the ions Ca, Ba, Sr, Ti, or  $\text{Fe}^{+++}$ . A similar method, claimed by P. Malozemoff, M. W. McAfee, and M. W. Kirk (Assrs. to Pacific Coast Borax Co.),<sup>101</sup> can be used for froth flotation of 73% of the borax from a pulped borate ore.

Two new developments in sodium silicate are a process covered by W. F. Wegst and J. H. Wills (Assrs. to Philadelphia Quartz Co.)<sup>102</sup> for the manufacture of a hydrated tetrasilicate (approximately  $\text{Na}_2\text{O}\cdot 4\text{SiO}_2\cdot 7\text{H}_2\text{O}$ ) by seeding at 60—90° a silicate solution of approximately the same ratio and 29—37% solids content, and the manufacture of silica sols containing about 3.5% of silica and only 0.05% of  $\text{Na}_2\text{O}$  described by J. W. Ryznar<sup>103</sup>; these sols are made by treating silicate liquors with ion-exchange resins, and are likely to find use in tanning and other industries.

Sodium hydride has recently become of more interest because of its use in fused caustic soda baths for cleaning metal strip; it can be made in such baths by interaction of sodium and hydrogen. Another method has been patented by F. Siegmann<sup>104</sup> which involves evaporating sodium metal in an electric arc between molten sodium electrodes in presence of hydrogen at 300°.

Sodium percarbonate can be made by treating sodium carbonate with hydrogen peroxide. In one process, that of V. W. Slater, W. S. Wood,

<sup>97</sup> *J.S.C.I.*, 1945, 64, 1; *B.*, 1945, I, 125.

<sup>98</sup> *J. Appl. Chem. Russ.*, 1944, 17, 337; *B.*, 1945, I, 327.

<sup>99</sup> *U.S.P.* 2,190,280; *B.*, 1945, I, 183.

<sup>100</sup> *U.S.P.* 2,310,315; *B.*, 1945, I, 22.

<sup>101</sup> *U.S.P.* 2,184,558; *B.*, 1945, I, 99.

<sup>102</sup> *U.S.P.* 2,179,806; *B.*, 1945, I, 62.

<sup>103</sup> *Ind. Eng. Chem.*, 1944, 36, 821; *B.*, 1945, I, 21.

<sup>104</sup> *U.S.P.* 2,313,028; *B.*, 1945, I, 184.



and B. Laporte Ltd.,<sup>105</sup> this treatment is carried out in presence of a saline mother-liquor from a previous precipitation, and in another process claimed by O. H. Walters and Imperial Chemical Industries, Ltd.,<sup>106</sup> the treatment is carried out in the cold in presence of diphenylguanidine as stabiliser.

#### OTHER ALKALI METAL COMPOUNDS.

Searches have been made for fresh sources of potash and for means for separating potash ores from crude minerals, such as by froth flotation. Potassium sulphate can be made from alunite by calcining, separating the resultant potash and alumina by leaching, and using the furnace gases to make sulphuric acid, which is caused to react with the potash.<sup>107</sup> Plentiful supplies of alunitic clay, described by M. L. Fitzgerald,<sup>108</sup> are available in the bed of Lake Campion, W. Australia. Polyhalite ( $K_2SO_4, MgSO_4, 2CaSO_4, 2H_2O$ ) can be used as a fertiliser providing a slowly soluble source of potassium sulphate, or it can be roasted to give a readily soluble potash. Processes for recovery of potassium carbonate and potassium sulphate from the roasted material have been studied in detail and the investigations have recently been reviewed by J. E. Conley and E. P. Partridge.<sup>109</sup> The ash of slate coke produced by the pyrolysis of alum slate to give shale oil contains 4—5% of potash, and J. A. Hedvall and S. Nordengren<sup>110</sup> recover 80—90% of this by calcining with limestone and salt and extracting with water. In the digestion of wood pulp with aqueous magnesium bisulphite, with recovery of the latter, potash gradually accumulates in the liquor and, according to R. S. Hatch (Assr. to Weyerhaeuser Timber Co.),<sup>111</sup> can be recovered by evaporating to dryness and burning the residue. The conversion of potassium sulphate into carbonate by the formate process has been carried on since 1938 and details are given by E. Wiedbrauck.<sup>112</sup> Aqueous potassium sulphate and milk of lime are treated with producer gas containing 30—32% of carbon monoxide at 30 atmospheres and above 200° to avoid the formation of double sulphates; calcium sulphate is filtered off and the potassium formate solution is oxidised to carbonate.

Lithium compounds are being obtained from Searles Lake in the form of  $Li_2NaPO_4$  and G. P. Alexandrov<sup>113</sup> describes how they can also be obtained by fusion of spodumene ( $Li_2O$  2.9%) at 1000° with equal parts of sodium and potassium sulphates. The electrolysis of Solikamsk

<sup>105</sup> B.P. 568,754; B., 1945, I, 255.

<sup>106</sup> B.P. 565,653; B., 1945, I, 62.

<sup>107</sup> B.P. 569,008; B., 1945, I, 256.

<sup>108</sup> *Chem. Eng. Min. Rev.*, 1945, 37, 241; B., 1945, I, 327.

<sup>109</sup> *U.S. Bur. Mines*, 1944, *Bull.* 459; B., 1945, I, 254.

<sup>110</sup> *Th. Svedberg. Anniv. Vol.*, 1944, 113; B., 1945, I, 152.

<sup>111</sup> U.S.P. 2,308,364; B., 1944, I, 397.

<sup>112</sup> *Chem. Technik*, 1942, 15, 188; B., 1945, I, 152.

<sup>113</sup> *J. Appl. Chem. Russ.*, 1944, 17, 183; B., 1945, I, 219.



carnallite for the manufacture of magnesium, details of which are given by E. A. Nikitina and A. G. Kogan,<sup>114</sup> leaves a residue containing 0.057% of rubidium and caesium chlorides from which rubidium and caesium can be recovered by precipitation with silicomolybdic acid, followed by treatment with ammonia to remove the silica, and recovery of the molybdic oxide as the quinoline salt.

### CALCIUM COMPOUNDS.

Lime and calcium carbonate are involved in many industries, and the types of kiln used vary considerably. In beet sugar manufacture, it has been proposed by R. M. Daniels (Assr. to Holly Sugar Corporation)<sup>115</sup> to dry and calcine the precipitated calcium carbonate in two stages using indirect and then direct heat so as to provide a source of carbon dioxide suitable for carbonating beet juice. B. L. Corson (Assr. to G. & W. H. Corson Inc.)<sup>116</sup> describes one method of slaking lime to give a dry, free-flowing powder by using a slight excess of water in a closed vessel, allowing the pressure to rise to 600 lb. per sq. in. for a few minutes, and then releasing the pressure. A plastic hydraulic lime is made by W. E. Carson<sup>117</sup> by slaking lime with enough water to keep the temperature below 82°, removing some of the water from the milk, and adding enough finely ground lime to make dry calcium hydroxide and again keeping the temperature below 82°. Calcium carbonate and sulphate are used as fillers in paints, rubber, newsprint, and other substances. R. R. McClure and J. P. Seguin (Assrs. to Diamond Alkali Co.)<sup>118</sup> claim that one such filler can be made by carbonating a solution of calcium hydroxide in an aqueous saccharide. Plant details have been given by H. R. Davidson<sup>119</sup> for the manufacture of a newsprint filler by carbonating slaked lime; the magnesium content of the filler should be low because of its alkalinity. R. W. Sullivan (Assr. to E. I. Du Pont de Nemours & Co.)<sup>120</sup> gives a method of restraining the crystal growth which is undesirable for pigment purposes by treating a carbonated lime suspension with a soluble glycolate. The production of a calcium sulphate filler from gypsum by dehydrating it and then hydrating with water in presence of a crystal growth restrainer such as gelatin, soya-lecithin, or methylcellulose, and subsequently calcining at 600—900°, is claimed by W. W. Heckert (Assr. to E. I. Du Pont de Nemours & Co.)<sup>121</sup> Calcium silicate also is used as a rubber filler, but it may affect the rate of vulcanisation due to the presence of small proportions of soluble calcium compounds; R. P.

<sup>114</sup> *J. Gen. Chem. Russ.*, 1941, 11, 877; B., 1945, I, 220. *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 509; B., 1945, I, 98.

<sup>115</sup> U.S.P. 2,194,164; B., 1945, I, 292.

<sup>116</sup> U.S.P. 2,309,168; B., 1945, I, 99.

<sup>117</sup> U.S.P. 2,193,391; B., 1945, I, 256.

<sup>118</sup> U.S.P. 2,188,663; B., 1945, I, 153.

<sup>119</sup> *Pulp & Paper Mag. Canada*, 1945, 46, 205; B., 1945, I, 183.

<sup>120</sup> U.S.P. 2,177,269; B., 1944, I, 397.

<sup>121</sup> U.S.P. 2,177,254; B., 1944, I, 397.



Allen (Assr. to B. F. Goodrich Co.)<sup>122</sup> proposes to remove these by treatment with aqueous carbon dioxide or a soluble carbonate, and then washing and drying the material.

Anhydrite reduction provides an industrial source of sulphur dioxide and a residue which is suitable for cement. Investigations have recently been carried out by E. Briner and C. Knodel<sup>123</sup> on the effect of water vapour at above 1000° on the reduction of natural and artificial anhydrite, and it has been found that the presence of water vapour permits the reaction to be carried out at 1300° to give about 90% reduction, whereas the same result is only achieved at 1450° in absence of water vapour.

Calcium hypochlorite is a convenient form of bleach of high available chlorine content. It is made by chlorinating milk of lime, which, under appropriate conditions, yields a normal or a basic hypochlorite solid and a solution of calcium chloride. One of the difficulties is to obtain the hypochlorite in a sufficiently coarse crystal form to be able to filter it. In a process patented by Mathieson Alkali Works (Assces. of H. L. Robson)<sup>124</sup> the chlorination is preferably carried out in two stages, the first of which readily yields good crystals of basic hypochlorite  $\text{Ca}(\text{OCl})_2 \cdot 2\text{Ca}(\text{OH})_2$ , which are filtered off from the solution; in the second stage, filterable crystals of normal hypochlorite are obtained by feeding equivalent amounts of chlorine and a slurry of basic hypochlorite continuously to a neutral reaction mixture at 10–25°.

#### OTHER ALKALINE-EARTH COMPOUNDS.

Strontium is available as celestine ( $\text{SrSO}_4$ ), and a study has been made by B. S. Srikantan<sup>125</sup> of its recovery as carbonate by a reduction process. The process involves compacting into blocks with salt and charcoal using starch as binder, reduction by subjecting to a bright red heat for an hour, lixiviating, and treating with sodium carbonate solution. A product containing 98% of strontium carbonate can be obtained.

Barium also occurs in nature as its sulphate, and many methods have been devised to recover it as soluble compounds. One method, described by S. S. Bhatnagar, S. Parthasarathy, and A. L. S. Rao,<sup>126</sup> involves heating it with excess of calcium chloride, and extracting the product with aqueous methyl alcohol, whereby 55% of the barium is recovered as chloride. Another method involves reduction with pulverised coal at 1100° for 4 hours, lixiviation of the barium sulphide so made, and chlorination to give 65–90% yield of barium chloride; the by-product sulphur is contaminated with barium sulphate formed by oxidation of the barium sulphide.

There is considerable interest in the recovery of magnesium from

<sup>122</sup> U.S.P. 2,314,188; B., 1945, I, 223.

<sup>123</sup> *Helv. Chim. Acta*, 1944, 27, 1406; B., 1945, I, 97.

<sup>124</sup> B.P. 565,089; B., 1945, I, 22.

<sup>125</sup> *J. Sci. Ind. Res. India*, 1944, 3, 62; B., 1945, I, 97.

<sup>126</sup> *Ibid.*, 108; B., 1945, I, 97.



dolomite, largely for conversion into magnesium metal or for use as refractories. Magnesia can be obtained from calcined dolomite by dissolving out the lime with ammonium chloride solution, and it has been suggested by P. Budnikov and I. I. Rivlin<sup>127</sup> that the process is economical if it is combined with the recovery of ammonia from the ammonium chloride liquor of the ammonia-soda process, and if the magnesia is converted into a refractory silicate. Another method of separating the magnesia and lime in calcined dolomite is by carbonation of an aqueous slurry, whereby magnesium is dissolved as its bicarbonate and insoluble calcium carbonate remains; the magnesia is then recovered as basic carbonate by boiling the solution, and the optimum conditions and mechanism of this boiling operation have been investigated by S. K. Wei.<sup>128</sup> Another method of separation, put forward by J. A. Murray (Assr. to Warner Co.),<sup>129</sup> is to dissolve out the calcium content as calcium hydrosulphide by treatment with hydrogen sulphide. Calcined dolomite can of course be used for absorbing carbon dioxide, and a suitable material for removing carbon dioxide from water without slaking is made by F. Tschirner (Assr. to Medford Engineering Co.)<sup>130</sup> by partly calcining dolomite granules at 780—880° and then quenching to 250°.

As magnesium metal is now largely made by electrolysis of fused magnesium chloride, the direct production of the chloride from burnt dolomite is advantageous. This can be done by a process described by J. M. Avery and R. F. Evans<sup>131</sup> involving carbonation in presence of calcium chloride solution, whereby calcium carbonate equivalent to all the calcium and magnesium in the burnt dolomite is formed and filtered off, leaving a magnesium chloride solution which is evaporated. Another method, of which details are given by E. E. Wrege and C. J. Anstrand,<sup>132</sup> is carbonation of the lime with carbon dioxide followed by dissolution of the magnesia with hydrochloric acid, purification of the magnesium chloride solution, and concentration by submerged combustion. The hydrated magnesium chloride must be dehydrated, and Mathieson Alkali Works (Assees. of J. L. Wood and R. B. MacMullin)<sup>133</sup> achieve this by fusion in presence of a halide diluent in an atmosphere of chlorine or hydrogen chloride gas.

#### ALUMINIUM COMPOUNDS.

Aluminium compounds are extracted from bauxite and other minerals chiefly for use in making aluminium, as alumina catalysts, and as

<sup>127</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 210; B., 1945, I, 98.

<sup>128</sup> *J. Chinese Chem. Soc.*, 1944, **11**, 34; B., 1945, I, 220.

<sup>129</sup> U.S.P. 2,317,396; B., 1945, I, 222.

<sup>130</sup> U.S.P. 2,317,961; B., 1945, I, 100.

<sup>131</sup> *Chem. Met. Eng.*, 1945, **52**, No. 4, 94; B., 1945, I, 220.

<sup>132</sup> *Chem. Industries*, 1945, **56**, 234; *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 1; B., 1945, I, 182.

<sup>133</sup> B.P. 569,186; B., 1945, I, 256.



aluminium sulphate or sodium aluminate for water treatment. The principal method of extraction is by treating it with concentrated caustic soda solution and filtering off the insoluble iron and other compounds as "red mud." A high silica content of the bauxite leads to losses of alkali and alumina in the red mud, and this can be avoided by ore-dressing methods for removing the silica or by sintering the bauxite with lime and sodium carbonate at 1000—1100° followed by aqueous extraction of the sodium aluminate.<sup>134</sup> F. R. Archibald and C. F. Jackson<sup>135</sup> describe how fusing with limestone at 1350° followed by leaching with caustic soda solution may be used with clays, but the limestone should be free from magnesium carbonate. J. H. Walthall, P. Miller, and M. M. Striplin have developed from the laboratory plant to the pilot-plant scale a sulphuric acid process for producing alumina from clay.<sup>136</sup> The clay is calcined and extracted with 40% sulphuric acid, and the filtered aluminium sulphate is electrolysed to remove iron and concentrated to 55%. It is then calcined in a rotary kiln and desulphurised for recovery of sulphur dioxide, leaving a residue containing 99% of alumina. A. Fleischer<sup>137</sup> describes how alunite ore can be used to make potash alum, which is hydrolysed at above 150° by direct injection of steam and then calcined to give alumina and potassium sulphate, and the latter is removed by leaching; this initial hydrolysis avoids the formation of sticky pyrosulphates during the calcination.

For catalytic purposes, alumina is required in special forms. Houdry Process Corporation<sup>138</sup> have shown that alumina of high stability and resistance to disintegration can be made by precipitation, ageing, drying, and pelleting; these pellets may then be impregnated with a molybdate and used as an alumina-molybdenum oxide catalyst. A. Stewart and Imperial Chemical Industries<sup>139</sup> have shown that alumina for chromatographic purposes can be made from alumina which has been activated by heating, by deactivating it with 1—10% of water. The General Electric Co.<sup>140</sup> manufacture free-flowing powdered alumina by igniting a highly hydrated sulphate such as ammonium alum at a temperature sufficient to give only  $\gamma$ -alumina, and tumbling the product in a vessel containing no other loose solids. Shell Development Co.<sup>141</sup> have several patents covering the impregnation of alumina with aluminium chloride vapour at 220—275° in a countercurrent tower or by heating in a closed vessel with aluminium chloride under pressure; alumina catalysts may also be supported on silica gels, or may sometimes be used in the form of activated clay or bauxite.

<sup>134</sup> *Chem. Met. Eng.*, 1945, 52, No. 1, 106; B., 1945, I, 183.

<sup>135</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1706; *Met. Tech.*, 11, No. 5; B., 1945, I, 153.

<sup>136</sup> *Trans. Amer. Inst. Chem. Eng.*, 1945, 41, 55; B., 1945, I, 220.

<sup>137</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1713; B., 1945, I, 153.

<sup>138</sup> B.P. 568,978; B., 1945, I, 256.

<sup>139</sup> B.P. 565,405; B., 1945, I, 62.

<sup>140</sup> B.P. 563,636; B., 1944, I, 365.

<sup>141</sup> B.P. 564,346; U.S.P. 2,311,712-3 and 2,313,053; B., 1944, I, 397; 1945, I, 23.



## COMPOUNDS OF OTHER METALS.

*Boron.*—A process for conversion of natural borates such as asharite by heating with hydrogen phosphates and subsequent neutralisation with copper carbonate or ammonia to yield boric acid and a phosphatic fertiliser is described by S. I. Volfkovitsch and L. E. Berlin<sup>142</sup>; clay borates can be treated by this method.

Crystalline boric oxide can be made, according to L. McCulloch (Assr. to Westinghouse Electric & Manufacturing Co.),<sup>143</sup> by heating boric acid until 10—12% of water remains in the viscous mass, which is then maintained at 220—250° for 1—30 days until the whole is completely solid.

*Cobalt.*—Details have been given by B. du Faur<sup>144</sup> of the experimental plant used for working up cobalt ore containing Co 23.75, Cu 25, Si 3, and pyrites 48%. After grinding, the ore was roasted and calcined, mixed with sulphuric acid to give 5% excess, and the mixture heated in an iron tank until a strongly fuming dry mass was obtained; this was leached with cold water and the iron oxidised by air, after which limestone was added to precipitate ferric hydroxide. The sulphates in solution were filtered and dried with sodium carbonate until all the copper was precipitated as basic copper carbonate and finally the cobalt was precipitated from the boiling solution by adding some sodium carbonate to avoid an excess and prevent co-precipitation of calcium and magnesium; the copper precipitate contained 7% of cobalt.

*Manganese.*—The concentration of manganese from low-grade ores, by using the reaction  $\text{MnO}_2 + 2\text{NO}_2 = \text{Mn}(\text{NO}_3)_2\text{aq.}$  followed by evaporation of the solution and recovery of manganese dioxide by the reverse reaction, has been studied on a semi-pilot-plant scale.<sup>145</sup> Starting with an ore containing 13—14.5% of manganese, the final product contains about 50% of manganese.

The electrodeposition of manganese dioxide on graphite anodes, for use in the electrical industry, has been studied by O. W. Storey, E. Steinhoff, and E. R. Hoff.<sup>146</sup> A dense, hard, deposit of manganese dioxide, which does not disintegrate, is obtained by electrolysing manganese sulphate solutions, in hot acid solution and with a potential drop across the cell less than the decomposition potential of water, acidified with sulphuric acid. When the manganese sulphate bath is neutral, or nearly so, higher voltages can be used, but the manganese dioxide then contains some lower oxides.

*Nickel.*—A process for recovery of nickel by chlorination is described

<sup>142</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, 43, 249; B., 1945, I, 182.

<sup>143</sup> U.S.P. 2,186,257; B., 1945, I, 184.

<sup>144</sup> *Chem. Eng. Min. Rev.*, 1942, 35, 14; B., 1945, I, 291.

<sup>145</sup> U.S. Bur. Mines, 1945, *Tech. Paper* 674; B., 1945, I, 255.

<sup>146</sup> *Trans. Electrochem. Soc.*, 1944, 86, *Preprint* 14, 183; B., 1945, I, 61.



by D. P. Bogatski,<sup>147</sup> who says that nickel silicate ores can be effectively extracted by chlorination, though less readily than nickel oxide. Garnierite is attacked to the extent of 4% at 300°, 90% at 900°, and 100% at 1150°. The efficiency of the process is increased by admixture of recovered ore but is practically independent of nickel content and the presence of moisture. For industrial purposes, either repeated chlorination at 400° and removal of the chlorides by leaching with water or chlorination at 800° and removal of chlorides in the vapour phase is recommended.

*Titanium.*—Although several patents have been taken out describing different methods of preparing titanium dioxide for pigments, none of these shows any development of note over existing methods. An interesting new application of chromium, vanadium, and titanium oxides is in the manufacture of electrical conductors. It is claimed by E. Wainer and N. R. Thielke<sup>148</sup> that materials having low or medium resistance, high power factor and dielectric constant, and a large negative temperature coefficient are made by calcining (a) chromic oxide 6—79 and titanium dioxide 94—21% at above 1095°, (b) vanadium pentoxide 6.8—82 and titanium dioxide 93.2—18% at above 925°, in an oxidising atmosphere, for a time sufficient to ensure the mass being of a uniform black colour.

*Tungsten.*—The recovery of tungsten from flotation concentrates containing 8—15% of tungsten oxide as scheelite is described.<sup>149</sup> As they cannot be further concentrated by flotation they are digested with sodium carbonate at 190° and 200 lb. per sq. in. in large autoclaves of a special design. The discharge from the autoclaves is allowed to cool to deposit silica, alumina, and antimony oxide and after filtration is treated with dry lime to precipitate the tungsten as calcium tungstate, which is filtered, off, washed, and roasted to give a product containing 65% tungsten oxide.

H. W. Highriter and W. C. Lilliendahl (Assrs. to Westinghouse Electric & Manufacturing Co.)<sup>150</sup> describe the production of tungsten oxide suitable for reduction to metal for lamp filaments by leaching ground wolframite concentrate with caustic soda, filtration, diluting, cooling, clarifying, and digesting with sodium peroxide to oxidise sulphides. After filtration, the solution at 80° is run through fine jets into 25% hydrochloric acid at 80° and vigorously stirred with the addition of concentrated nitric acid to prevent reduction. The reaction mixture is diluted to approximately 3% hydrochloric acid and the precipitate is collected and washed.

<sup>147</sup> *J. Appl. Chem. Russ.*, 1944, 17, 346; B., 1945, I, 328.

<sup>148</sup> U.S.P. 2,311,917; B., 1945, I, 24.

<sup>149</sup> *Chem. Eng. Min. Rev.*, 1944, 37, 54; B., 1945, I, 292.

<sup>150</sup> U.S.P. 2,316,583; B., 1945, I, 223.



## INDUSTRIAL GASES.

As the last review was made in the 1942 report the present review covers the years 1943-5 inclusive. The manufacture of water-gas, producer gas, coal gas, and other fuel gases is not covered in this section, and gases such as ammonia, sulphur dioxide, chlorine, and nitrogen oxides are considered in other appropriate sections.

Quite an appreciable amount of work has been done on hydrogen manufacture which is probably a reflexion of the war demand for hydrogen and its compounds. The processes are very varied.

Developments for electrolytic processes and for the production of hydrogen include a new type of cell which is in use at Trail. It is described by B. P. Sutherland<sup>151</sup> and its characteristic features are a concrete top supporting the electrodes, with asbestos diaphragms and collecting skirts; the cost of the cell is claimed to be a little over half that of older types and its life is at least six years. Another advantage is that the operating voltage of the cells is reduced by the addition of 0.5 g. of vanadium pentoxide per litre of electrolyte. Another variation<sup>152</sup> is the production of electrolytic hydrogen under pressures of 125-175 lb. per sq. in. which is considered by J. S. Just.<sup>153</sup>

A number of processes based on the reaction of hydrocarbon with steam over a catalyst to produce a carbon monoxide-hydrogen mixture which is subsequently converted into a carbon dioxide-hydrogen mixture have been reported. The Girdler Corporation<sup>154</sup> produce small quantities of pure industrial hydrogen by passing hydrocarbons with steam over a nickel catalyst contained in externally heated tubes. The process is now being used in the U.S.A. and the hydrogen produced competes with electrolytic hydrogen. This corporation<sup>155</sup> have also designed a mobile hydrogen generator which employs the reaction between steam and alcohol; the hydrogen is used for balloon filling and the by-product carbon dioxide can be used for fire-fighting. Another development of interest is the use of reactions between carbon dioxide and hydrocarbons to produce carbon monoxide and hydrogen. These gases may be converted into carbon dioxide and hydrogen and the carbon dioxide after separation can be recirculated. Claims for a process based on this reaction have been made by the Oil & Gas Research, Inc.<sup>156</sup> A modification of this process has been patented by M. W. Kellogg Co.,<sup>157</sup> who introduce the carbon dioxide into the reaction by bubbling the hot hydrocarbon gas through ethanalamine solutions of carbon dioxide.

<sup>151</sup> *Trans. Electrochem. Soc.*, 1944, **85**, 183; B., 1944, I, 305. See also U.S.P. 2,293,594.

<sup>152</sup> B.P. 570,233; B., 1945, I, 329.

<sup>153</sup> *J. Inst. Elect. Eng.*, 1944, **91**, Part I, 382; B., 1945, I, 21.

<sup>154</sup> *Petrol Refiner*, 1945, **24**, No. 9, 119.

<sup>155</sup> *Chem. Met. Eng.*, 1944, **51**, No. 9, 161.

<sup>156</sup> U.S.P. 2,322,989; B., 1945, I, 213.

<sup>157</sup> U.S.P. 2,185,989; B., 1945, I, 100.



The steam-iron process for hydrogen manufacture was developed in Britain during the war to provide hydrogen for balloon filling. The efficiency of this process has been greatly improved and the ratio  $(\text{H}_2 + \text{CO in water-gas})/(\text{H}_2 \text{ made})$  has been reduced to 1.3. This method of hydrogen production has been described by W. K. Hutchinson,<sup>158</sup> who gives capital and running costs and discusses the theoretical basis of the process. Mechanical improvements for removing oxides of carbon are claimed by the Power Gas Corporation.<sup>159</sup> An unusual process involving the reaction between iron or iron-copper alloy and liquid water under pressure at 230—370° is proposed by M. W. Kellogg Co.<sup>160</sup> in which the finely-divided metal is fed continuously into the reaction vessel and the spent material removed continuously for regeneration with a reducing gas containing carbon monoxide, hydrogen, etc. before recirculation.

The manufacture of hydrogen from water-gas is described by C. Berthelot.<sup>161</sup> After conversion of carbon monoxide into carbon dioxide, the latter is removed by washing with water and the remaining carbon monoxide is removed by copper solutions; the economics of converting carbon monoxide at 1 atm. and 20 atm. are compared. The Gas Research Board<sup>162</sup> claims the use of a molybdenum sulphide sulphur-tolerant catalyst working at about 300° to obtain conversion of carbon monoxide into dioxide with steam, and V. Kondrateev and M. Ziskin<sup>163</sup> have studied this reaction in quartz tubes, obtaining evidence that it can occur as a chain reaction in the purely homogeneous phase.

The production of oxygen by electrolysis is usually referred to along with the production of electrolytic hydrogen. Production of oxygen by the liquefaction of air has also been further developed and is the subject of several patents. According to Linde Air Products Co.<sup>164</sup> storage losses are reduced by sub-cooling liquid oxygen before storage by expanding a liquid containing nitrogen obtained from the plant. Many sweeping claims have been made for the Kapitza process for liquefying air, but H. Hausen<sup>165</sup> expresses the opinion that a successful large-scale plant using the process would not achieve a very great reduction in the cost of liquid air and would have even less effect on the cost of production of oxygen gas on a large scale. The Kapitza process<sup>166,167</sup> derives all the required cooling effect through isentropic expansion of air through a special high-speed turbine, which is claimed to have a high efficiency at low pressure (6—7 atm. gauge), above that of piston expansion machines operating from high pressures (40—220 atm.), as used in other

<sup>158</sup> *Gas World*, 1945, 123, 105, 204.

<sup>159</sup> B.P. 538,348, 548,183, 548,183, 548,397-8; B., 1942, I, 86; 1943, I, 157, 405.

<sup>160</sup> U.S.P. 2,182,747; B., 1944, I, 398.

<sup>161</sup> *Chim. et Ind.*, 1943, 49, 313.

<sup>162</sup> B.P. 549,838; B., 1943, I, 202.

<sup>163</sup> *Acta Physicochim. U.R.S.S.*, 1943, 18, 197; A., 1944, I, 253.

<sup>164</sup> U.S.P. 2,321,445; B., 1945, I, 154.

<sup>165</sup> *Z. ges. Kälte-Ind.*, 1941, 48, No. 2, 24.

<sup>166</sup> *Avto-gen. Delo*, 1941, 12, No. 5, 25.

<sup>167</sup> *J. Physics U.S.S.R.*, 1939, 1, 7; see also *Ann. Repts.*, 1941, 28, 58.



processes; even so Kapitza himself only claims that in a large-scale plant, which was not then built and has not since been reported on, the power consumption would be 1.1 kw.-hr. per kg. of liquid air, compared with 1.3 kw.-hr. per kg. from the Heylandt process, although additional advantages in capital cost might result from the use of lower pressures. In the manufacture of oxygen gas from liquid air, however, the main energy consumption is for rectification and not for refrigeration, and adequate refrigeration is provided in the Linde-Frankl process by compression of only 6—8% of the air to 200 atm. Thus the use of Kapitza's process for liquefaction is unlikely to reduce greatly the cost of oxygen gas, as obtained in large Linde-Frankl plants. Apparently nothing has been published about Kapitza's proposed process for the separation of gaseous oxygen, and final judgment must be reserved until details are known. However, if Kapitza's claim for a highly efficient turbine can be substantiated in a large-scale machine then this could have an important effect on the cost of liquid oxygen or in other gas-separation work.

In the U.S.A. liquefied carbon dioxide is now distributed as such on a large scale, and the design of a low-pressure tank wagon is described by C. A. Getz and E. Geertz.<sup>168</sup>

Some improvements are claimed in processes for obtaining carbon dioxide from industrial gases. According to R. Gibbs, carbon dioxide may be economically recovered from rotary limekiln gases, and the method in which soda ash is employed for removing carbon dioxide from gases has been improved by obtaining a suspension of sodium bicarbonate which is decomposed at a temperature below the boiling point of liquor.<sup>169</sup> Instead of soda ash, a potassium borate solution is employed by the American Potash & Chemical Corporation.<sup>170</sup> Carbon dioxide is readily obtained by scrubbing ammonia synthesis gases with water under pressure and its recovery by a two-stage let-down process from the water is considered theoretically by H. L. Seifert and J. D. B. Ogilvie.<sup>171</sup>

C. E. Peck<sup>172</sup> describes exhaustively the many different kinds of inert atmospheres which can be made from fuel gases and anhydrous ammonia, covering chemistry, cost, equipment, and applications. In a "Symposium on controlled atmospheres" E. E. Slowter<sup>173</sup> gives details of equipment, instruments, and operation, together with costs.

The American process for recovering helium from natural gas, containing 1—7% of helium, has been described editorially<sup>174</sup>; all the gases except helium are liquefied and removed; operations in Texas have

<sup>168</sup> *Ind. Eng. Chem.*, 1941, **33**, 1124; B., 1942, I, 6.

<sup>169</sup> U.S.P. 2,183,324; B., 1944, I, 398. Also U.S.P. 2,256,962 and B.P. 538,866.

<sup>170</sup> U.S.P. 2,374,876.

<sup>171</sup> *Canad. Chem.*, 1944, **28**, 665; B., 1945, I, 61.

<sup>172</sup> *Ind. Heating*, 1943, **10**, 336, 479, 799, 951, 1118.

<sup>173</sup> *Trans. Amer. Soc. Metals*, 1942, 176.

<sup>174</sup> *Chem. Met. Eng.*, 1944, **51**, No. 6, 92; B., 1944, I, 364.



also been described.<sup>175</sup> L'Air Liquide Soc. Anon.<sup>176</sup> claim a process for the manufacture of pure krypton in which krypton is removed from a large quantity of pre-cooled air by scrubbing with the nitrogen-oxygen mixture obtained from the main rectifying column.

The commercial manufacture of hydrogen sulphide from sulphur and hydrocarbons has been described by R. F. Bacon and E. S. Boe<sup>177</sup>; at 250° heavy fuel oil reacts with sulphur to give a high yield of hydrogen sulphide, and at 600—650°, in the presence of a catalyst, sulphur reacts quantitatively with methane and steam to form hydrogen sulphide and carbon dioxide.

Acetylene and ethylene are becoming of increasing importance as starting materials for industrial organic syntheses.<sup>178</sup> Although calcium carbide remains the chief source of acetylene, processes for manufacture from hydrocarbons are coming into use. Y. Mayor<sup>179</sup> reviews the various methods of making both acetylene and ethylene. Manufacture of acetylene by partial combustion of hydrocarbons is a process which is being developed; contrary to other authorities, N. I. Kobozev<sup>180</sup> states quenching after cracking is not necessary, and in fact yields may be increased appreciably by omitting quenching. The Wulff Process Co.<sup>181</sup> claims an improved apparatus, as do Air Reduction Co.<sup>182</sup> and Phillips Petroleum Co.<sup>183</sup> J. J. Kündig and E. Briner<sup>184</sup> conclude that the use of arcs struck between carbon electrodes in an atmosphere of hydrogen has no technical value; the maximum yield of acetylene was only 2.4 g. per kw.-hr. Ethylene is being manufactured by cracking of hydrocarbons and from alcohol and by recovery from coke-oven gas. The Pure Oil Company<sup>185</sup> claim a process for catalytic cracking from ethane, propane, and butane, and recovery from coke-oven gas by liquefaction is described by J. Wucherer<sup>186</sup> and C. Berthelot.<sup>187</sup>

<sup>175</sup> *Amer. Gas J.*, 1945, **162**, No. 5, 49.

<sup>176</sup> G.P. 727,107.

<sup>177</sup> *Ind. Eng. Chem.*, 1945, **37**, 469; B., 1945, I, 328.

<sup>178</sup> *Canad. Chem.*, 1944, **28**, 657.

<sup>179</sup> *L'Ind. Chim.*, 1941, **28**, 45.

<sup>180</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 261.

<sup>181</sup> U.S.P. 2,343,866 and 2,319,679; B., 1945, II, 95.

<sup>182</sup> U.S.P. 2,179,378-9; B., 1944, I, 358.

<sup>183</sup> U.S.P. 2,377,245.

<sup>184</sup> *Helv. Chim. Acta*, 1942, **25**, 1251; A., 1943, I, 95.

<sup>185</sup> U.S.P. 2,354,892.

<sup>186</sup> *Z. Ver. deut. Ing. Verfahrenstech.*, 1943, No. 1, 21.

<sup>187</sup> *Chim. et Ind.*, 1941, **45**, Spec. No., March, 38.



## GLASS.

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THE amount of published work which is reviewed in this report is considerably in excess of that for previous years, and it is anticipated that the volume of work will be still greater in the next few years. Owing to the present difficulty of obtaining the published papers of the European countries, information is still lacking of any recent progress which has been made there, but there are indications that more scientific papers are now reaching this country.

### THE CONSTITUTION OF GLASSES AND SILICATES.

The light emitted by a fluorescent centre in fluorescent glasses can be utilised as an indicator of the location of the unit in the glass structure and the phenomenon of glass fluorescence is therefore a useful tool for the investigation of the constitution of glass. Changes in the surroundings of the unit under varying conditions may be studied, and the interpretation of these changes can be used in extending the evidence of X-ray analysis to the more complex glasses. N. J. Kreidl<sup>1</sup> has summarised the results of recent studies on the fluorescence of glass in conjunction with the modern theory of glass structure. He discusses the effects of the main constituents of glass on the intensity, wave-length, and width of the fluorescent bands. Fluorescence is favoured by the presence of a high proportion of glass-forming ions and by the presence of modifying ions of low field strength. If the fluorescent centres are atoms or molecules, for example, CdS or Ag, or cations  $Mn^{++}$ ,  $UO_2^{++}$ , and  $Ce^{+++}$ , or an anion  $UO_4^{---}$ , the intensity of the fluorescence is decreased and its wave-length shifted towards the red, the more the centre is disturbed by its surroundings. Increased symmetry of environment narrows the fluorescent bands. It is, therefore, possible to determine the structural differences between glasses and crystals of equal composition. The uranyl group  $UO_2^{++}$  is regarded as the most suitable fluorescent centre for intensity studies. Kreidl discusses the fluorescence of glasses containing rare-earth elements and manganese; in the case of manganese the effect of the base glass is described in detail. A section on the identification of optical glasses by observing their fluorescence under a bactericidal ultra-violet lamp emitting light of short wave-lengths is included.

For many years glass technologists have applied the terms "acidic" and "basic" to glass-making substances, even though no hydrogen or hydroxyl ions are present. K. H. Sun and A. Silverman<sup>2</sup> suggest that

<sup>1</sup> *J. Opt. Soc. Amer.*, 1945, 35, 249; C., 1945, 285.

<sup>2</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 8; B., 1945, I, 154.



such terms may legitimately be used, as the Lewis acid-base theory can be applied to glass reactions; in such reactions, "acidic" substances are electron acceptors and "basic" substances electron donors. Several glass reactions are given in the form of equations in which electron sharing occurs.

M. L. Huggins and K. H. Sun<sup>3</sup> have discussed the additivity of energy in glasses. The energy of a solid such as a glass or a crystal containing only oxygen and electropositive elements is derived from the attractions between each positive atom and the surrounding oxygens. Since the number and arrangement of atoms around a positive atom do not vary much from compound to compound, and from glass to glass, the additivity of energies might be expected in such substances. Huggins and Sun compute energies relative to the energy of a dilute gas composed of charged ions and deduce energy constants for each component element in its usual oxygen environment. The constants may be related to the position of the elements in the periodic classification. Slight deviations from additivity which occur for silicates and phosphates appear to be related to the number of oxygens in the  $\text{SiO}_4$  and  $\text{PO}_4$  groups which are shared with neighbouring Si and P atoms.

The molecular structure of the vitreous state has been discussed by A. Smekal.<sup>4</sup> For the stability of the vitreous state, it is necessary that the binding energy permits a stable irregular atom arrangement, and Smekal suggests that there are three possible types of bonding giving rise to three simple kinds of glass, namely, glasses consisting of inorganic compounds in which ionic and atomic bonds are present, glasses containing semi-metallic elements, such as carbon and selenium in which metallic and atomic bonds are present, and organic glasses in which homopolar and intermolecular bonds exist.

Although the random network theory is now generally regarded as the most acceptable theory of the glassy structure, evidence for the crystallite theory is brought forward from time to time. S. K. Majumdar, B. K. Banerjee, and K. Banerjee<sup>5</sup> have recently carried out an X-ray study of the solution of alkali halides in borax and boric oxide glasses. In the case of sodium chloride in borax, the lines of sodium chloride appeared together with some extra lines which could not be identified with either sodium chloride or crystalline sodium borate. The results suggest that sodium chloride crystallites are present in the glass, but the origin of the unidentified lines has not been traced.

The results obtained by R. S. Krishnan and P. V. Rao<sup>6</sup> in a study of anomalous depolarisation in optical glasses using C. V. Raman's technique are interpreted as indicative of the existence of molecular aggregates in glasses.

<sup>3</sup> *J. Soc. Glass Tech.*, 1944, 28, 463r; A., 1945, I, 331.

<sup>4</sup> *Nova Acta Leopoldina*, 1942, 11, 511.

<sup>5</sup> *Nature*, 1945, 156, 423.

<sup>6</sup> *Proc. Indian Acad. Sci.*, 1944, 20, A, 109; A., 1945, I, 10.



## GLASS-MAKING MATERIALS AND STUDIES IN GLASS MELTING.

*Materials.*

Continuing his series of reviews on glass-making oxides, B. Schweig has described the specific effects of boric oxide,<sup>7</sup> zinc oxide,<sup>8</sup> and alumina<sup>9</sup> on melting and on physical and chemical properties. R. C. Vickery<sup>10</sup> has given an account of the uses of cerium and didymium oxides in glasses.

A method of removing iron from glass-making sands or other minerals has been patented<sup>11</sup>; the mineral is treated with an aqueous solution of titanous sulphate and an iron compound, followed by washing.

The effects on physical properties of replacing the lime by zirconia in a glass of composition  $\text{SiO}_2$  70,  $\text{Na}_2\text{O}$  13,  $\text{Al}_2\text{O}_3$  5, and  $\text{CaO}$  12% have been studied by M. Fanderlik and Z. Schaefer.<sup>12</sup> It was found that at  $1450^\circ$ , replacement of 4% of  $\text{CaO}$  by  $\text{ZrO}_2$  did not increase the melting time, although the viscosity of the glass was increased.

A method of preparing pebble-size nodules of batch has been patented.<sup>13</sup>

*Glass Melting.*

The results of a study on the effect of temperature on the homogenising rate of a soda-lime-silica glass ( $\text{SiO}_2$  73,  $\text{Na}_2\text{O}$  17,  $\text{CaO}$  10%) have been given by R. L. Tiede and F. V. Tooley.<sup>14</sup> Using the same mixture, a series of meltings was made at temperatures ranging from  $1232^\circ$  to  $1454^\circ$ , each melting having the same melting time of 4 hours. The presence of refractory was eliminated by using platinum crucibles and convection mixing was reduced to a minimum. The homogeneity was determined by measuring the density spread on each melt. The density spread decreased rapidly from  $1232^\circ$  to  $1288^\circ$ , becoming a minimum at  $1325^\circ$  and increasing slowly above that temperature. The major part of the spread was found to be concentrated in the top half of the melt; this was attributed to segregation. The spread could be reduced considerably by repeated pouring and re-melting. The authors suggest that convection currents in a glass tank are important in the improvement of homogeneity.

A. K. Lyle<sup>15</sup> has reported some experiments on the measurement of the fining time of glass. Under controlled conditions, a small charge of pulverised batch was added to a relatively large amount of melted and fined glass, and the fining time was related with temperature and with the glass viscosity. The results indicate that fining time is not a function

<sup>7</sup> *Glass*, 1945, 22, 9, 37, 69; B., 1945, I, 330.

<sup>8</sup> *Ibid.*, 99, 127; B., 1945, I, 330.

<sup>9</sup> *Ibid.*, 183; B., 1946, I, 263.

<sup>10</sup> *Metallurgia*, 1944, 30, 311.

<sup>11</sup> Pilkington Bros. and A. Sherlock, B.P. 555,241.

<sup>12</sup> *Sklarske Rozhledy*, 1943, 20, 41.

<sup>13</sup> G. J. Bair, U.S.P. 2,366,473.

<sup>14</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 42; B., 1945, I, 185.

<sup>15</sup> *Ibid.*, 282; B., 1946, I, 23.



of viscosity alone. Comparison of the results of the laboratory experiments with those obtained in full-scale tanks showed that fining time as found in the experiments varied directly as the time required to produce fined glass in a day tank. For continuous tanks, fining time could be correlated directly with the ratio of melting area to tons of glass produced, after correction had been made for differences in methods of temperature measurement in the tank and in the laboratory experiments. Curves showing melting area in sq. ft. per ton per day versus furnace temperature and melting rate in tons per 100 sq. ft. per days versus temperature are deduced.

It is well known that temperature gradients exist in the vertical direction in glass tanks. R. Halle and W. E. S. Turner<sup>16</sup> have recently measured the gradients in a number of commercial glasses melted in a small laboratory tank furnace. All the glasses were of the soda-lime-silica type, three containing the colouring constituents carbon-sulphur, iron-manganese, and ferrous iron yielding amber, dark green, and blue-green glasses respectively, and the remaining glass being colourless. Over the range of surface temperatures 1000—1400°, the gradients were found to be parallel, so that the diathermanous properties of the glasses are not affected by temperature. At any one temperature, the gradients were greatest in the surface layers up to 0.5—0.7 in. and the maximum gradient was found in the colourless glass. Below a depth of 1 in., the decrease in temperature was linear with depth. The application of insulation to the side walls and bottom of the tank reduced the gradients without affecting the differences in temperature distribution between the different glasses. Figures are given for the amounts of heat transmitted by the various glasses.

The value of statistical control charts constructed from daily measurements of specific gravity made during production from tanks has been demonstrated by L. G. Ghering,<sup>17</sup> who gives examples of charts obtained in ten glass tanks. The predominant cause of large fluctuations is usually found in the weighing of batch, other assignable causes being variations in cullet and raw materials, and changes in the furnace firing. It was found that cordiness grading could be correlated with range of density.

The effects of batch changes, the building up of temperature gradients, and the absence of bubbles in cullet melted several times on viscosity variations in tank glass and the consequent appearance of dead glass have been discussed.<sup>18</sup> The sources of bubbles and the manner in which they appear in blown glassware have been reviewed.<sup>19</sup>

C. A. Bradley<sup>20</sup> has discussed the problem of volatilisation from molten

<sup>16</sup> *J. Soc. Glass Tech.*, 1945, 29, 5T; B., 1945, I, 358.

<sup>17</sup> *J. Amer. Ceram. Soc.*, 1944, 27, 373; B., 1945, I, 127.

<sup>18</sup> Anon., *Ceram. Ind.*, 1944, 43, 60.

<sup>19</sup> Anon., *ibid.*, 76.

<sup>20</sup> *Bull. Amer. Ceram. Soc.*, 1944, 23, 379; B., 1945, I, 64.



glasses, considering the glasses as solutions of more or less volatile constituents. Applying Henry's law and Clapeyron's equation to published experimental results, the amount of volatile material lost by volatilisation in commercial melting units is calculated.

K. Endell and M. von Ardenne<sup>21</sup> have reported some observations on the sintering and fusion of glass mixtures, employing the electron microscope with a magnification of  $\times 2500$ . Quartz particles vitrified between  $1500^{\circ}$  and  $1600^{\circ}$  and batches of optical glass showed fusion phenomena at  $900$ – $1000^{\circ}$  depending on composition, but changes occurred at  $630^{\circ}$  and parts melted at  $890^{\circ}$ . In general, the batch particles were not sufficiently fine for practical conclusions to be drawn.

Two general papers on the decolorising of glass have been published. The first of these<sup>22</sup> deals with pot glass; the principles of decolorising are reviewed and the effects of the iron content of the raw materials, of oxidising and reducing agents in the batch, and of chemical and physical decolorisers are discussed. In the second paper,<sup>23</sup> dealing with tank glass, A. C. Ottoson emphasises the importance of choice of raw materials and care in handling. The effects of various chemical decolorisers and of oxidising conditions are given in the form of tables, and the uses of elemental selenium and of arsenic and neodymium oxides are discussed in particular. It is essential that accurate control of the furnace atmosphere should be maintained if repeatable results are to be obtained with given decolorisers.

#### *Devitrification.*

The influence of boric oxide on the crystallisation rate of a soda-potash-lime-silica glass of the general formula  $(75.82 - x)\text{SiO}_2$ ,  $x\text{B}_2\text{O}_3$ ,  $8.56\text{CaO}$ ,  $6.86\text{Na}_2\text{O}$ , and  $7.90\text{K}_2\text{O}$  has been investigated by G. E. Walker.<sup>24</sup> With increasing amounts of boric oxide the liquidus temperature was reduced from  $1110^{\circ}$  to  $875^{\circ}$  for  $5.44\%$   $\text{B}_2\text{O}_3$ . Further additions of boric oxide caused a slight rise in the liquidus followed by a fall to  $830^{\circ}$  at  $22.54\%$   $\text{B}_2\text{O}_3$ . Up to  $2.05\%$   $\text{B}_2\text{O}_3$ , the primary crystalline phase was tridymite, but above  $5.44\%$  the primary phase was devitrite; a phase boundary exists in glasses of intermediate composition. Variations in the rate of crystal growth with boric oxide content were found to follow closely the variations in liquidus temperature.

Some interesting data on the devitrification of Vycor have been provided by M. E. Nordberg.<sup>25</sup> Below  $900^{\circ}$  the devitrification rate is very low, but it becomes appreciable in the region of  $1000^{\circ}$  and up to  $1200^{\circ}$  is greater than that of fused silica. Above  $1200^{\circ}$  its rate falls progressively below that of fused silica. Devitrification starts with the formation of cristobalite.

<sup>21</sup> *Glastech. Ber.*, 1943, 21, 121.

<sup>22</sup> S. R. Scholes, *Bull. Amer. Ceram. Soc.*, 1944, 23, 468; B., 1945, I, 127.

<sup>23</sup> *Ceram. Ind.*, 1945, 44, 63, 66.

<sup>24</sup> *J. Soc. Glass Tech.*, 1945, 29, 38r; B., 1945, I, 359.

<sup>25</sup> *J. Amer. Ceram. Soc.*, 1944, 27, 299; B., 1945, I, 25.



The effects on liquidus temperature of substitutions of fluorine for silica and of phosphorus pentoxide for silica and dolomite lime in a soda-dolomite lime-silica glass have been reported.<sup>26</sup> No generalisations can be drawn from the data, but the presence of phosphorus pentoxide tends to cause opalescence in the working range.

C. E. Gould, J. Davies, and A. J. Holland<sup>27</sup> have reported the appearance of silicon stones in a tank glass melted from batch containing cullet contaminated with aluminium milk-bottle caps. The presence of elemental silicon was attributed to reduction by the aluminium and was confirmed by physical and chemical methods.

### *Furnaces and Refractories.*

There is very little fresh to report on the subject of furnace design, but some useful summaries on glass tank design have appeared during the year. R. S. Arrandale<sup>28</sup> has dealt in some detail with tank practice, including the procedure for heating up from cold, furnace operation, and an appraisal of points of fundamental importance in a number of specific furnaces. The heating-up programme should, of course, be determined by the rate of expansion of the refractories and Arrandale gives time-temperature curves for constant expansion rates ranging from 0.010 to 0.025 in. per foot per day. An expansion rate of 0.018 in. per foot per day is regarded as ideal. In dealing with furnace operation, the question of temperature distribution throughout the length of the tank is considered, and Arrandale concludes that the optimum position for the highest temperature relative to the bridge should be 0.45—0.55 of the length of the melting compartment.

F. G. Schwalbe<sup>29</sup> has considered the design, construction, and methods of operation of a continuous tank for hand-blown glass-ware. The instrumentation for fuel, air, furnace temperature, and pressure and measurement of glass level are discussed. In a second paper, Schwalbe has discussed methods of improving the design of tank furnaces.<sup>30</sup>

The improvements which may be effected by the use of automatic control of furnaces have been discussed in a number of papers. F. E. Early and W. H. Hasselbach<sup>31</sup> emphasise the beneficial effects obtained on overall furnace performance by using modern automatic equipment for controlling combustion and furnace pressure. The effects are demonstrated by the results given for fuel saving, reduction of furnace maintenance, and improved quality of product. E. G. Smith,<sup>32</sup> discussing automatic control and its effect on furnace design and operation, suggests methods of improving furnace design if full advantage of automatic

<sup>26</sup> Owens-Illinois Research Laboratories, *J. Amer. Ceram. Soc.*, 1944, 27, 369.

<sup>27</sup> *J. Soc. Glass Tech.*, 1945, 29, 35r; B., 1945, I, 359.

<sup>28</sup> *Glass Ind.*, 1945, 26, 19, 75, 128; B., 1945, I, 330.

<sup>29</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 151; B., 1945, I, 293.

<sup>30</sup> *Glass Ind.*, 1944, 25, 550; B., 1945, I, 127.

<sup>31</sup> *Bull. Amer. Ceram. Soc.*, 1945, 24, 16; B., 1945, I, 185; C., 1945, 98.

<sup>32</sup> *Ibid.*, 10; C., 1945, 152.



control is to be taken. A series of articles dealing with the firing of tank furnaces has appeared,<sup>33-35</sup> and in a further article<sup>36</sup> the importance of thorough batch mixing and the effects of automatically operated individual port controls and control of furnace atmosphere are discussed. A. E. Badger, G. H. Johnson, and J. H. Healy<sup>37</sup> have analysed the factors affecting the melting capacity of glass tanks. If melting capacity is exceeded, cords, seeds, and stones are liable to occur; the viscosity of the glass must be reduced if it is impractical to reduce rate of pull. Some effects of the use of moist batch are discussed.

W. Horak<sup>38</sup> has given examples of the ways in which stones and cords can be traced to the developments of faults in the tank, and W. L. Fabianac<sup>39</sup> is responsible for a valuable contribution on the same subject. He describes in detail the various types of stone which may appear in soda-lime glasses under operating conditions; stones arising from devitrification are discussed in addition to those arising from the refractories and from the batch. A comprehensive series of photomicrographs of the various stones is included in the paper.

A method of ensuring a supply of well refined homogeneous glass to the drawing compartment of a sheet glass tank has been patented.<sup>40</sup> The inhomogeneous glass near the walls is encouraged to enter a refining compartment where it cools and sinks to the bottom before returning to the main part of the tank. G. W. Batchell<sup>41</sup> has patented a method for eliminating batch dust incidental to charging a furnace; he envelopes the raw batch within a shell of molten glass. A patent on a method of drawing off glass through an electrically heated channel has been granted to G. Slayter.<sup>42</sup>

The phenomenon of "shelving" at the horizontal joints in tank blocks is well known, and it has been suggested that the glass-clay mixture resulting from the corrosion tends to sink because it is denser than the glass itself. Thus, downward-facing refractories are continuously washed by fresh glass which causes attack, while upward-facing refractories are not attacked. G. H. Johnson and A. E. Badger<sup>43</sup> have carried out experiments using test samples of refractories made from a suitable mixture of alumina and silica in such proportions that no density change took place on solution; they concluded that the type of attack is independent of the density effect since the downward-facing refractory was still attacked to a greater extent than an upward-face.

<sup>33</sup> C. Chaffer, *Ceram. Ind.*, 1944, **43**, 61.

<sup>34</sup> Anon., *ibid.*, 46.

<sup>35</sup> G. E. Seil, *ibid.*, 52.

<sup>36</sup> Anon., *ibid.*, 58.

<sup>37</sup> *Ibid.*, 1945, **44**, 118.

<sup>38</sup> *Ibid.*, 60.

<sup>39</sup> *J. Amer. Ceram. Soc.*, 1944, **27**, 330; B., 1945, I, 64.

<sup>40</sup> W. F. Gaunder, U.S.P. 2,363,954.

<sup>41</sup> U.S.P. 2,371,213.

<sup>42</sup> U.S.P. 2,188,927; B., 1945, I, 155.

<sup>43</sup> *Glass Ind.*, 1944, **25**, 404; B., 1945, I, 128.



J. Boow and G. E. Walker<sup>44</sup> have investigated the variation in apparent porosity in commercial slip-cast sillimanite tank blocks. Measurements on 45 specimens taken from one block showed a variation of 18.9—21.4%, and further measurements were made after repeated firings for successive periods of 3 hours each at 1500°. A gradual decrease in apparent porosity with firing time was observed. It is suggested that variations may be due to temperature variations during firing, variations in chemical composition due to inadequate mixing, and to differences in the extent of crack development in various parts of the block, possibly arising from variations in heating rate.

A. Ottoson and C. J. Uhrmann<sup>45</sup> have suggested methods for improving glass-house pots. Low porosity improves the life of the pots and yields a better-quality glass, and may be attained by correct grog grading, using finer grog, and by correct choice of bonding clay. New pot materials such as porcelain and dense bodies, using materials such as feldspar, talc, and alumina, are discussed. The paper includes a description of modifications in pot design to accommodate cast-in liners and changes which may be introduced to permit better melting by studying the currents in the glass during melting.

The laboratory testing of glass-house refractories has always been a controversial subject, and the methods used are rather arbitrary. R. K. Smith<sup>46</sup> has discussed the significance of a testing programme for such refractories. He divides refractory failure into two general types, one due to heat alone and the other to heat plus contamination. The first may be determined by a sagging test with a bar  $1 \times 1 \times 10$  cm. supported cantilever fashion in an electric furnace; the test gives the temperature of failure and the rate of failure at various temperatures. In measuring the rate of attack by molten glass on refractories, the importance of temperature control is emphasised. The refractory samples must be representative of the refractory it is desired to test. The use of ground cullet in place of raw batch for the corroding medium has been found to give identical results under carefully duplicated experimental conditions. A similar discussion by S. M. Phelps<sup>47</sup> has appeared in which the test data are related to the manufacture and use of the refractory product.

R. G. Abbey<sup>48</sup> advocates the use of unburned basic brick, for example, chrome brick or magnesite, in regenerators and superstructures. According to his experience, such bricks resist slagging by batch dust carried over into the regenerators. He describes some practical applications of the use of unburned basic bricks.

G. S. Fulcher and T. E. Field<sup>49</sup> have patented a composition of a cast

<sup>44</sup> *J. Soc. Glass Tech.*, 1944, 28, 152T; B., 1945, I, 64.

<sup>45</sup> *Bull. Amer. Ceram. Soc.*, 1944, 23, 385; B., 1945, I, 64.

<sup>46</sup> *Ibid.*, 457.

<sup>47</sup> *Ibid.*, 310; C., 1945, 14.

<sup>48</sup> *Glass Ind.*, 1945, 26, 279; B., 1945, I, 330.

<sup>49</sup> U.S.P. 2,352,530.



zirconia refractory suitable for glass. It consists substantially of zirconia together with at least one of the alkalis  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , or  $\text{K}_2\text{O}$ , the total alkali content being not more than 15%. The refractory is substantially free from alumina.

#### ANALYSIS AND TESTING OF GLASS AND GLASS-MAKING MATERIALS.

The technique of analysing glass batches for segregation of materials has been discussed by H. J. Hunt.<sup>50</sup> The most important factors are size of sample and the effect of cullet, 20—30-g. samples being taken, which were reduced to 10—20 g. after removal of cullet. Hunt recommends that the results should be calculated on a cullet-free basis, and he discusses a method of correcting for cullet. An example is given of an investigation of two borosilicate batches to determine whether they differed in respect of segregation in practice; the batches were calculated to give the same glass but differed in their ingredients. Soda and boric oxide were determined and these percentages calculated on a cullet-free basis.

Many descriptions of analytical procedures have appeared throughout the year and those reviewed in this section have been chosen for their possible applications in glass analysis. Of the general analytical methods, S. Zerfoss and R. L. Hess<sup>51</sup> have described some qualitative spot tests for common glass constituents using organic reagents and the technique of Feigl. The technique of non-destructive sampling by scratching the glass against a quartz plate is described; it is claimed that amounts of material of the order of 1  $\mu\text{g}$ . can be dealt with. Many minerals and such refractories as fused alumina, porcelain, and sillimanite can be brought into solution by heating with the halogen acids at 300° under pressure and the technique for carrying out the procedure has been described.<sup>52</sup> L. L. Merritt and J. K. Walker<sup>53</sup> consider that 8-hydroxyquinoline is a more selective reagent than 8-hydroxyquinoline for certain ions, and they discuss the effect of pH on the completeness of the precipitation of the hydroxyquinoline complexes of cupric, ferric, zinc, and magnesium ions. M. Niessner and F. Hecht<sup>54</sup> have rechecked some previously reported micro-analytical procedures for glass-colouring elements, in order to determine the limits of accuracy of the methods and the effect of interfering elements. They deal with nickel in the presence of cobalt, manganese in the presence of lead, copper, and zinc, selenium in the presence of gold, and the determination of uranium. A quantitative spectrographic method for the analysis of small powder samples has been described by E. J. Fitz and W. M. Murray.<sup>55</sup>

<sup>50</sup> *J. Amer. Ceram. Soc.*, 1944, **27**, 305; C., 1945, 14.

<sup>51</sup> *Ibid.*, 1945, **28**, 16; C., 1945, 98.

<sup>52</sup> C. L. Gordon, W. G. Schlecht, and E. Wichers, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 451; C., 1945, 212.

<sup>53</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 387; C., 1944, 195.

<sup>54</sup> *Glastech. Ber.*, 1943, **21**, 228.

<sup>55</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 145; C., 1945, 197.



A method for determining silica in aluminous materials using the molybdenum-blue reaction has been described,<sup>56</sup> and two methods have been put forward for the estimation of small amounts of silica. The first of these<sup>57</sup> involves the reduction of the silicomolybdate complex to the intense molybdenum-blue; the quantities and concentrations specified for the reagents are optimum for colour-stability, sensitivity, and speed of colour development. In the second method, M. F. Adams<sup>58</sup> employs the yellow molybdisilicic complex; the method is claimed to be reproducible to within  $\pm 1\%$  for a sample containing 0.5 mg. of silica. The spectrophotometric determination of calcium, which is precipitated as oxalate and determined as permanganate, has been described,<sup>59</sup> and G. H. Osborn<sup>60</sup> has given details of a method of estimating calcium in the presence of barium and strontium. J. J. Lingane<sup>61</sup> has described a volumetric method for calcium based on the oxalate-permanganate procedure; the method permits a direct determination to be made in the presence of silica, iron, aluminium, magnesium, and phosphorus, and the accuracy is stated to compare favourably with that of the classical methods which require the removal of most of the elements mentioned.

Among the procedures described for the estimation of the alkalis, M. F. Adams and J. L. St. John<sup>62</sup> employ potassium chloroplatinate. F. R. Bacon and D. T. Starks<sup>63</sup> have applied the Rogers and Caley periodate method for lithium to the determination of sodium and potassium in silicates. The use of hydrofluoric and perchloric acids as a decomposition mixture in the determination of potassium and sodium in silicates has been investigated by G. G. Mervin and L. B. Woolaver<sup>64</sup>; the method avoids the major difficulties of the Lawrence Smith and Berzelius methods. A solution of all the metallic elements in the sample is prepared, perchlorates being formed which yield a solid mixture on evaporating to dryness. The thermal decomposition of the mixture separates sodium, potassium, and calcium from magnesium, iron, and aluminium, the latter forming oxides and the alkalis forming soluble chlorides. The method is not applicable to samples containing sulphates.

F. C. Guthrie and J. T. Nance<sup>65</sup> have suggested that the accuracy of the determination of the alkaline-earth metals by direct titration using phenolphthalein as indicator can be improved by adding to the neutral

<sup>56</sup> J. A. Brabson, I. W. Harvey, G. E. Maxwell, and O. A. Schaeffer, *ibid.*, 1944, 16, 705; C., 1945, 90.

<sup>57</sup> A. L. Olsen, E. A. Gee, V. McLendon, and D. D. Blue, *ibid.*, 462; C., 1945, 5.

<sup>58</sup> *Ibid.*, 1945, 17, 542; C., 1946, 6.

<sup>59</sup> R. E. Scott and C. R. Johnson, *ibid.*, 504; C., 1946, 3.

<sup>60</sup> *Analyst*, 1945, 70, 207; C., 1945, 224.

<sup>61</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 39; C., 1945, 187.

<sup>62</sup> *Ibid.*, 435; C., 1945, 222.

<sup>63</sup> *Ibid.*, 230; C., 1945, 221.

<sup>64</sup> *Ibid.*, 554; C., 1946, 1.

<sup>65</sup> *J.S.O.I.*, 1945, 64, 50; C., 1945, 87.



solution of the alkaline-earth chloride or nitrate, before titration, an equal volume of acetone.

The determination of iron in glass-making sands by spectrographic methods has been investigated by L. H. Ahrens,<sup>66</sup> who uses silicon as an internal standard; the presence of potassium was found to lead to high results due to the pronounced depressant effect of potassium on the silicon spectrum. M. Kennard and C. R. Johnson<sup>67</sup> have given transmittance data for the ferric complex of sulphosalicylic acid at various pH values; the measurement at pH 8.2 is the most sensitive and this pH value gives the most stable colour. A colorimetric thiocyanate method for the determination of iron in the presence of cobalt has been described by E. A. Brown.<sup>68</sup>

A. M. Mitchell and M. G. Mellon<sup>69</sup> have investigated spectrophotometrically the colorimetric method for nickel which involves the formation of a soluble red complex obtained by treating the nickel ion in ammoniacal solution with dimethylglyoxime; transmittance curves are given. C. Carruthers<sup>70</sup> has given data for the polarographic determination of copper using salicylaldehyde as a reagent. The polarographic determination of manganese as trihydrogen pyrophosphatomanganate has been suggested by J. I. Watters and I. M. Kolthoff,<sup>71</sup> pyridine in aqueous solution with strong acid being used to precipitate iron, vanadium, chromium, and cerium; there is no appreciable coprecipitation of manganese provided a previous reduction with sulphite and oxidation with nitric acid is carried out.

K. G. Stone and N. H. Furman<sup>72</sup> have estimated magnesium by polarographic measurement of the excess of 8-hydroxyquinoline which remains after precipitation of the magnesium salt, and a method for magnesia in magnesite and dolomite has been put forward.<sup>73</sup>

A colorimetric micro-method for vanadium based on the oxidation of benzidine in 10N-phosphoric acid, which yields an intense yellow coloration, has been described by I. P. Alimarin<sup>74</sup>; it is claimed that a dilution of 1 : 5,000,000 can be detected. Microchemical methods for vanadium and chromium have been described by B. I. Frid.<sup>75</sup>

Of the methods available for phosphorus, R. E. Kitson and M. G. Mellon<sup>76</sup> have given details of a spectrophotometric study of the molybdo-vanadophosphoric acid method. The phosphovanadomolybdate method

<sup>66</sup> *J. South Afr. Chem. Inst.*, 1944, 27, 28; C., 1945, 95.

<sup>67</sup> *Proc. Trans. Texas Acad. Sci.*, 1944, 27, 45; C., 1945, 160.

<sup>68</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 228; C., 1945, 229.

<sup>69</sup> *Ibid.*, 380; C., 1945, 230.

<sup>70</sup> *Ibid.*, 398; C., 1945, 223.

<sup>71</sup> *Ibid.*, 1944, 16, 187; C., 1944, 161.

<sup>72</sup> *Ibid.*, 596; C., 1945, 77.

<sup>73</sup> A. J. Boyle, C. C. Casto, and R. M. Haney, *ibid.*, 313; C., 1944, 155.

<sup>74</sup> *J. Appl. Chem. Russ.*, 1944, 17, 83; C., 1945, 158.

<sup>75</sup> *Zavod. Lab.*, 1945, 11, 17.

<sup>76</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 379; C., 1945, 9.



has been described for the determination of phosphorus in limestone.<sup>77</sup> A new method for the analysis of phosphate glasses has been put forward by Z. Schaefer.<sup>78</sup>

The determination of fluorine by both gravimetric and volumetric methods has been described.<sup>79</sup> For the gravimetric method, fluorine is precipitated as calcium fluoride from dilute acetic acid solution buffered with sodium acetate. The volumetric method consists of precipitation of the fluorine as lead chlorofluoride and back-titration of the excess of sodium chloride.

The use of tannin as a selective reagent for zirconium has been studied by W. R. Schoeller<sup>80</sup> and a rapid and accurate method for the estimation of tin using silicomolybdate has been described.<sup>81</sup>

A sensitive spot test for cerium using a saturated aqueous solution of *p*-phenetidine which yields a violet colour with  $Ce^{+++}$  in solution has been published.<sup>82</sup>

#### ANNEALING.

Problems in annealing fall into two general classes, one being concerned with the development of a high refractive index in the glass and the other with the removal of mechanical stress. Further work under both headings has been reported during the course of the year.

A detailed study of the variation with time and temperature of the refractive index of a borosilicate glass in the annealing region has been described by H. A. McMaster.<sup>83</sup> An empirical equation for chilled glass at constant temperature is derived, and is of the form

$$\{1/(N_e - N)\} - \{1/(N_e - N_0)\} = At,$$

where  $N_e$  = equilibrium index,  $N_0$  = initial index,  $N$  = index at time  $t$ , and  $A$  is related to the absolute temperature by the expression  $\log A = (K/T) + C$ , where  $K$  and  $C$  are constants. The expression for variation of index with time is similar to that proposed by Adams and Williamson for rate of strain release and has been interpreted by N. W. Taylor as indicating the presence of bimolecular reactions. An exponential relation for variation of index has been proposed by Winter, but McMaster considers that his expression agrees more closely with the experimental data. The value of  $K$  gives the activation energy per Avogadro's number of elementary processes and the value derived by McMaster is of the same order of magnitude as that derived by other workers for rate of strain release, viscosity variations, and delayed elastic effects in other glasses.

<sup>77</sup> J. A. Brabson, J. H. Karchmer, and M. S. Katz, *ibid.*, 553; C., 1945, 8.

<sup>78</sup> *Glastech. Ber.*, 1943, 21, 46.

<sup>79</sup> R. Geyer, *Z. anorg. Chem.*, 1943, 252, 42; C., 1945, 94.

<sup>80</sup> *Analyst*, 1944, 69, 259; C., 1945, 5.

<sup>81</sup> I. Baker, M. Miller, and R. S. Gibbs, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 269; C., 1944, 157.

<sup>82</sup> P. Wenger, Y. Rusconi, and R. Duckert, *Helv. Chim. Acta*, 1944, 27, 1479; C., 1945, 89.

<sup>83</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 1; B., 1945, I, 154.



A. Q. Tool<sup>84</sup> has derived an empirical equation for stress relaxation during annealing. The equation is based on Maxwell's equation for viscous flow, but allowance is made for the change in viscosity which occurs when glass anneals at constant temperature. The derived equation fits the experimental data of Adams and Williamson and appears to be more suitable than the reciprocal relation proposed by them.

The question of release of stress from glass at room temperature has always been controversial. L. G. Ghering and T. D. Green<sup>85</sup> have recently examined the degree of permanence of strains in a number of standard strain discs which were prepared in 1938 for the Glass Container Association of America. Thirtysix discs were examined after a period of seven years, the results being treated statistically. After allowing for observational and instrument errors, the change in strain was estimated to be not greater than  $\pm 1.3\%$ . This change is too small to affect the utility of the standards in practical use, but it was considered that the order of accuracy of measurement was too low for any further conclusions to be drawn. In a short note which follows the paper by Ghering and Green, F. W. Preston<sup>86</sup> suggests that while their mathematical argument shows that the change was not more than  $\pm 1.3\%$ , on physical considerations any change must be very much less than the quoted figure, and he considers that viscous flow at room temperature is unlikely.

A projection strain viewer for use with small objects, particularly glass-glass and glass-metal seals, has been described by J. Fortey.<sup>87</sup>

#### DURABILITY.

M. E. Nordberg has given some data on the chemical stability of Vycor 790.<sup>25</sup> This glass is extremely stable to all acids except hydrofluoric, but even in this case is eight times as resistant as Pyrex to cold 60% hydrofluoric acid. Vycor is particularly well suited to high-precision analytical work since contamination of solutions by substances leached from the glass is extremely small. Owing to its high softening point it can be used for many ashing, ignition, and calcining operations. *In vacuo*, no reaction occurs between Vycor and metals below nickel in the electromotive series at temperatures up to 1150°, but electropositive metals in the molten state react with it.

In their work on the effect of replacing silica by fluorine or phosphorus pentoxide, the Owens-Illinois Research Laboratories have determined the effects on durability.<sup>26</sup> Thus, the resistance to 0.02N-sulphuric acid is increased for small substitutions of fluorine for silica, but the change in resistance when phosphorus pentoxide replaces silica is not measurable. Replacement of dolomite lime by phosphorus pentoxide decreased the durability. Similar results were obtained for resistance to distilled water,

<sup>84</sup> *J. Res. Nat. Bur. Stand.*, 1945, **34**, 199; B., 1945, I, 331.

<sup>85</sup> *J. Amer. Ceram. Soc.*, 1945, **28**, 288; B., 1946, I, 24.

<sup>86</sup> *Ibid.*, 295; B., 1946, I, 24.

<sup>87</sup> *J. Soc. Glass Tech.*, 1945, **29**, 124r; C., 1945, 285.



but in this case the replacement of dolomite lime by phosphorus pentoxide did not decrease the resistance.

Data on the durability and thermal endurance of laboratory glasses developed in Russia have been given in the summary of a paper by M. A. Bezborodov.<sup>88</sup>

Methods of removing alkali from the surface of glass to improve durability and increase electrical resistance have been reviewed by H. S. Williams and W. A. Weyl.<sup>89</sup> In addition to the known methods, they describe a new method of base exchange in which they employ kaolin or other clays in which the amount of replaceable hydrogen is high. The reactions may be accomplished at temperatures between 150° and 600°, and the method has the advantage that it may be used on finished glassware.

F. L. Jones<sup>90</sup> has discussed the deterioration of glass in tropical use. Water, either as liquid or vapour, is responsible for the deterioration, and the chemical factors governing the deterioration in the tropics are similar qualitatively to those in more temperate regions, but the degree of damage is greater as high humidity favours the growth of plant and insect life. Under exceptional conditions, water may condense on the surface to form a concentrated alkaline solution which attacks the silica, the glass becoming pitted or etched. On the other hand, the condensed water may dissolve carbon dioxide and the dilute carbonic acid solution etches glasses containing less than 60% of silica, leaving a hydrated silica layer which shrinks and cracks on drying. Iridescence is an interference phenomenon produced by a hydrated silica layer too thin to crack away from the glass. If organic matter is present on the surface, simple forms of animal and plant life may grow, and these often produce organic acids which attack the glass.

A method of improving the durability of sheets of soda-lime and lead plate glass, described as a "fortification" process, has been patented by F. W. Adams.<sup>91</sup> The surfaces are exposed for 1—3 days to an atmosphere near the saturation point, the glass being at a temperature above the dew point. The surface polish deteriorates and is restored by treatment with a dilute mineral acid, followed by baking for 5—15 minutes at 100—300°.

#### PHYSICAL PROPERTIES.

##### *Density and Thermal Expansion.*

In his summary of the properties of Vycor, M. E. Nordberg<sup>25</sup> has given some data on the density and thermal expansion of this glass compared with fused silica. The thermal expansion coefficient is  $7.5 \times 10^{-7}$  for Vycor 790 compared with 33 and  $5.5 \times 10^{-7}$  for Pyrex

<sup>88</sup> *Trans. All-Union Conf. Anal. Chem.*, 1943, 2, 431; *Glass Ind.*, 1945, 26, 228; C., 1945, 217.

<sup>89</sup> *Glass Ind.*, 1945, 26, 324; B., 1946, I, 133.

<sup>90</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 32; B., 1945, I, 154.

<sup>91</sup> U.S.P. 2,377,062.



and fused silica respectively. Owing to its low thermal expansion, Vycor may be heated to redness and plunged into water without fracture.

The investigation of the Owens-Illinois Research Laboratory on the effects of replacing silica and dolomite lime by phosphorus pentoxide in a soda-dolomite lime-silica glass<sup>26</sup> shows that substitution of 1%  $P_2O_5$  for 1%  $SiO_2$  decreases density by 0.0077 g. per c.c.; the corresponding density change for dolomite lime is a decrease of 0.0248 g. per c.c.

K. H. Sun and H. W. Safford<sup>92</sup> have summarised published data on the density and thermal expansion of glasses in the system  $Na_2O-SiO_2$  within the temperature range 900—1400°. After an examination of the methods of measurement employed, Sun and Safford conclude that the most reliable data are those published by Heidtkamp and Endell for six soda-silica glasses, and they show that for each of these glasses there is a linear relation between specific volume and temperature, that is, the coefficient of expansion is constant for a given composition. Equations are derived connecting specific volume and temperature, one for glasses with 40—50% (weight) of  $SiO_2$  and the other for 50—80% of  $SiO_2$ .

Routine measurement of density is often carried out as a check on the uniformity of the product from glass tanks and M. A. Knight<sup>93</sup> has discussed the magnitude of the errors which can occur if the effects of temperature and air buoyancy are ignored in the measurements. The paper includes examples of the calculation of densities determined by Archimedes' method and the sink-float method using liquid mixtures.

Methods of melting glasses at 2000° devised by J. H. Partridge were reviewed in the 1944 Reports, and a glass of low thermal expansion ( $8-15 \times 10^{-7}$ ) made by such methods has now been patented.<sup>94</sup> The glass contains a small amount of barium oxide so that its electrical conductivity at 2000° is sufficiently low for electric current to pass through the glass to provide part of the heat necessary for melting. Glasses of high expansion for sealing to alloys and metals of high expansion have been patented by H. Fischer<sup>95</sup>; an example of such a glass is  $SiO_2$  44.25,  $Al_2O_3$  5,  $BeO$  2,  $MgO$  6,  $BaO$  3,  $ZnO$  3.5,  $CaO$  0.25,  $Na_2O$  27.5, and  $K_2O$  8.5%.

#### *Thermal Endurance.*

An apparatus for testing simultaneously the thermal endurance of a large number of tumblers or beakers has been described by M. R. Savitskii.<sup>96</sup> The test articles are filled automatically with boiling water which falls at constant velocity from a fixed height. After cooling to 65° for blown ware and 55° for pressed ware, the articles are quenched in water at 20°.

<sup>92</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 11; B., 1945, I, 154.

<sup>93</sup> *Glass Ind.*, 1945, 26, 173; B., 1945, I, 331.

<sup>94</sup> B.P. 568,469; B., 1945, I, 258.

<sup>95</sup> G.P. 728,308.

<sup>96</sup> *Legkaya Prom.*, 1941, 1, 54.



*The Strength of Glass.*

Several investigations on the mechanical strength of glass have been reported during the year under review, and a number of these are due to J. B. Murgatroyd. In dealing with the mechanism of brittle rupture in glass, Murgatroyd<sup>97</sup> utilises data given by various investigators to test the Griffith "crack" theory and the weak molecular bond theory of the strength of glass; he concludes that modifications to the theory are required to cover the known facts. It is suggested that Griffith's flaws consist of pockets of quasi-viscous material surrounded by larger three-dimensional aggregates, and that when the viscous material has yielded to an applied stress, it no longer sustains a load and becomes the equivalent of a "hole" in the glass; such a "hole" would act as a point of stress concentration. On this hypothesis the time which elapses before breakage occurs is explained as due to the time required for the relaxation of stress in the quasi-viscous material. Using a mechanical model to represent a pocket, Murgatroyd derives an equation relating breaking strength with time and values calculated from it are shown to agree with published experimental results.

In two further papers, Murgatroyd<sup>98,99</sup> discusses the strength of glass fibres. Reduction in fibre diameter decreases the Young's modulus and the rigidity modulus. The rigidity modulus of fibres heated to 400° is increased, but no increase in Young's modulus is observed until the temperature is increased to 520°. The viscosity of the glass is increased with increases in the elastic moduli. These results are interpreted as being due to changes in the constitution of glass on drawing into fibre, and it is suggested that long chains of molecules lie parallel with the direction of drawing; lateral bonds between the chains are few. Heat-treatment at low temperatures permits the formation of some lateral bonds resulting in a stiffening of the structure. At higher temperature levels the chain structure should break up, but is prevented from doing so on account of the dimensions of the very fine fibres. The experimental methods for the determination of the elastic moduli at various temperatures are described. Young's modulus is determined by measuring the deflexion of a 1-cm. length of fibre resting on knife edges with a rider at the centre; the oscillating-disc method was used to determine the rigidity modulus. In the second part of the paper, the effect of heat-treatment on strength is discussed and it is shown that the distribution curves for breaking strains are comparable with a random distribution of flaws which increase in number when the fibres are heated. The strength of the fibres on heat-treatment tends towards that for massive glass.

H. E. Powell and F. W. Preston<sup>100</sup> have investigated the tensile strength

<sup>97</sup> *J. Soc. Glass Tech.*, 1944, 28, 406r; B., 1945, I, 293.

<sup>98</sup> *Ibid.*, 368; B., 1945, I, 293.

<sup>99</sup> *Ibid.*, 388; B., 1945, I, 293.

<sup>100</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 145; B., 1945, I, 293.



of massive glass by measuring the load which must be applied to a steel ball in contact with the glass in order to form a pressure cone crack. The area stressed was of the same order as the area of cross-section of a glass fibre, and it was found that the strengths obtained were comparable with those normally obtained with fibres. This suggests that the abnormally high strengths of fibres are not due to the orientation of a chain structure.

In another publication, F. W. Preston<sup>101</sup> points out that the experimental results relating strength of glass with the duration of stressing yield a linear relation if reciprocal stress is plotted against the logarithm of the time of duration of a steady load. Extrapolation of the relation implies that the stress which can be supported for infinite time is zero, and that no finite stress can break the glass if the duration of the load is less than 6 micro-seconds. No physical explanation is given, but the report is regarded as a preliminary to a more detailed paper.

Continuing his work on the strength of glass, R. N. Haward<sup>102</sup> has reported the results of an investigation of the behaviour of laminated and toughened glass under static loading and under impact at different velocities. Under a small bending force, the difference in behaviour was not very great, but under large bending stresses, toughened glass was found to be the stronger, having about twice the strength of ordinary sheet glass. At low-velocity impact (less than 10 m.p.h.) from a heavy object, the probability of the object breaking up the material and passing through it was not very different for similar pieces of toughened and laminated glass, but at impact velocities greater than 20 m.p.h. the resistance of laminated glass was greater than that of toughened glass. The results also show that toughened glass is simply a material which breaks like ordinary sheet glass, but in which a constant stress must be added to the stress required to break it in any given time.

W. A. Weyl<sup>103</sup> has reviewed the literature on the effect of surface treatment on the strength of glass and, in particular, the effect of acid gases during annealing. He suggests that the metakaolin process for the removal of alkali might be used to increase the mechanical strength as well as the chemical durability; the process might be applied in cases where tempering is inconvenient.

A summary of a paper by N. Krotova<sup>104</sup> on the mechanical strength of bare and coated glass fibres has been published.<sup>105</sup> For bare fibres of 20  $\mu$ . thickness, Young's modulus was 3800 kg. per cm.<sup>2</sup>, and their ultimate tensile strength was 86 kg. per mm.<sup>2</sup> Fibres coated with rubber behaved similarly to bare fibres, probably because rubber adhered poorly to the glass. Fibres coated with films (less than 1  $\mu$ . thick) of

<sup>101</sup> *Nature*, 1945, **156**, 55.

<sup>102</sup> *J. Soc. Glass Tech.*, 1944, **28**, 133T; B., 1945, I, 64.

<sup>103</sup> *Glass Ind.*, 1945, **26**, 369; B., 1946, I, 133.

<sup>104</sup> *J. Tech. Phys. U.S.S.R.*, 1944, **14**, 455.

<sup>105</sup> *Glass Ind.*, 1945, **26**, 418.



various polymerised materials, urea-formaldehyde or vinylite resin were found to have a greater elongation under a given stress and the tensile strength diminished below 80 kg. per mm.<sup>2</sup> These effects depended on the thickness of the coating. Statistical analysis of the results showed that the fibres became more uniform in respect of mechanical properties after being coated.

J. E. Ablard<sup>106</sup> has investigated the conditions which must be met if labels of ceramic colours applied to glass bottles are to "fit" the glass without the development of strain in the glass itself. A special thermal endurance test was used which tested the strength of the body of the labelled bottle without producing large strains in the base. Ablard found that in order to minimise the strain set up when both bottle and label are cooled to room temperature, the ceramic colour must have the slightly lower thermal expansion.

According to M. E. Nordberg,<sup>25</sup> the strength of Vycor is similar to that of normal glasses.

#### *Softening Point, Viscosity, and Surface Tension.*

An improved apparatus for the fibre elongation method for the determination of softening point has been described by A. H. Falter.<sup>107</sup> J. T. Littleton defined softening point as the temperature at which a uniform thread of glass 23.5 cm. long and 0.55—0.75 mm. diameter, suspended vertically in a furnace of specified characteristics, will elongate at the rate of 1 mm. per minute under its own weight, the rate of heating being 5—10° per minute. Falter has investigated the utility of the method over a wide range of temperatures and glass conditions. He describes his improved apparatus in detail and results are given for repeat measurements on several glasses. Results of individual tests on homogeneous specimens varied from 1° to 6°; variation in specimen diameter was found to affect the results slightly.

M. E. Nordberg<sup>25</sup> measured the softening point of Vycor 790 by the fibre method and found it to be 700° above that of Pyrex and only 150° below that of fused silica.

In addition to the effect on other properties, the Owens-Illinois Research Laboratories have investigated the effect on viscosity of replacement of SiO<sub>2</sub> by F and of SiO<sub>2</sub> and CaO, MgO by P<sub>2</sub>O<sub>5</sub>.<sup>26</sup> The purpose of the investigation was to determine whether important working properties can be maintained by the addition of other materials to the batch when the amount of soda ash in the batch is reduced. The fluorine replacement was found to reduce the viscosity appreciably and probably increases the working range. The replacement of silica by phosphorus pentoxide had little effect on viscosity but the viscosity was increased when the dolomite lime was replaced.

An experimental survey of the elastic and viscous properties of a soda-

<sup>106</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 189; B., 1945, I, 331.

<sup>107</sup> *Ibid.*, 5; C., 1945, 142.



lime-silica glass at temperatures below the annealing range has been carried out by G. O. Jones.<sup>108</sup> Test strips were cut from drawn sheet and measurements made on centrally loaded beams of rectangular cross section; the development of strain under applied stress was observed. The results obtained showed that at quite low temperatures the strain is made up of an elastic part which is completely reversible, plus a delayed viscous part. The reversible elastic part may be divided into an instantaneous component and a delayed component which appears rapidly at first and then approaches asymptotically a maximum value. The total delayed elastic strain for a given applied stress is a function of temperature. At temperatures approaching the transformation point, it became difficult to separate the instantaneous and delayed parts of the elastic strain. Viscosities as high as  $10^{17.8}$  were measured; such values are substantially higher than any measured values previously reported for glass.

Observations made by W. G. Martin and F. W. Lauck<sup>109</sup> on glass coatings on split steel rings suggest that there is no plastic flow of glass at room temperature. After the rings were coated some were split immediately and others were split one to two years later. Compressive forces in the glass caused similar distortion of the rings in both cases, indicating the absence of flow in the glass.

Using published data on the surface tensions of glasses, K. H. Sun and H. W. Safford<sup>110</sup> have calculated the parachors of glasses in the system  $\text{Na}_2\text{O}-\text{SiO}_2$  in the temperature range  $900-1400^\circ$ . The parachor  $\phi$  is given by the expression  $MV\sigma^{1/4}$ , where  $M$  is molecular weight,  $V$  specific volume, and  $\sigma$  surface tension; it is an additive function of chemical composition. Sun and Safford compute the parachor factors of each glass constituent and using the property of additivity calculate the specific parachor  $V\sigma^{1/4}$  for the  $\text{Na}_2\text{O}-\text{SiO}_2$  system. The specific parachor was found to vary linearly with temperature, and a temperature coefficient of 0.000093 specific parachor unit per  $^\circ\text{C}$ . found over a wide range of compositions. Equations are given for the specific parachors of glasses in the system.

In the same paper, viscosity data for glasses in the same system are analysed; the measurements made by H. R. Lillie are utilised. It is suggested that the plot of  $\log \eta$  against  $1/\theta$ , where  $\theta$  is the temperature in  $^\circ\text{C}$ ., gives a better straight line than the corresponding plot using the reciprocal of the absolute temperature. Equations are given for  $\log$  viscosity in terms of percentage weight and moles of the silica constituent.

H. Jebsen-Marwedel<sup>111</sup> has suggested that surface tension is the most important factor in the fusion of glass particularly for the disappearance of striæ. He has described experiments using glasses of different colours and different surface tensions and beads of the glasses were mixed and

<sup>108</sup> *J. Soc. Glass Tech.*, 1944, **28**, 432T; B., 1945, I, 331.

<sup>109</sup> *J. Amer. Ceram. Soc.*, 1944, **27**, 352; B., 1945, I, 64.

<sup>110</sup> *Ibid.*, 1945, **28**, 11; B., 1945, I, 154.

<sup>111</sup> *Glastech. Ber.*, 1943, **21**, 57.



fused together in platinum dishes. The manner of distribution of the different glasses in one another was determined by their mutual wetting action.

### *Electrical Properties.*

The measurement of the electrical conductivity of a glass containing less than 68% of silica has been described by F. L. Cornish.<sup>112</sup> Direct-current measurements were made at 1.5—67.5 volts on a test piece 12.5 mm. diameter and 46 mm. long over a temperature range 200—650°. The log specific resistance plotted against reciprocal absolute temperature gave a linear relation with a transformation point at 527° c.

The electric properties of Vycor 790 have been given by M. E. Nordberg,<sup>25</sup> comparisons with Pyrex and fused silica being included.

H. C. Steiner<sup>113</sup> has reviewed the uses of glass in electronic tubes, summarising the properties and applications of glass for the electronics industry. The available American glasses are discussed from the point of view of glass-metal seals and their electrical resistivities.

The uses of fibre glass in electrical insulation have been reviewed by J. M. Robertson.<sup>114</sup>

### *Optical Properties.*

In addition to publications on optical glasses which have appeared, data on filter glasses which do not contain colouring agents are reviewed in this section. Coloured glasses, whether for optical filters or otherwise, are discussed in the next section.

There is very little up-to-date information on the values of the stress optical coefficient and the recent investigation by W. Balmforth and A. J. Holland<sup>115</sup> is to be welcomed on this account alone. After reviewing earlier measurements, these workers describe their measurements on three series of glasses: (a) soda-lime-silica glasses of general formula  $6\text{SiO}_2, (2-x)\text{Na}_2\text{O}, x\text{CaO}$ , (b) seven optical flint glasses, and (c) five optical barium crown glasses. In the first series, replacement of soda by lime resulted in a small increase in the stress optical coefficient. The measurements on the flint glasses were in agreement with those of F. Pockels, indicating zero stress optical coefficient for a glass containing 75% of lead oxide. In the third series, the coefficient decreased with increasing barium content.

The transmission properties of Vycor 790 have been published.<sup>25</sup> This glass is highly transparent in the visible spectrum and has a very high transmission down to a wave-length of 365 m $\mu$ ., the transmission falling to zero—10% at 254 m $\mu$ . in a 2-mm. thickness. Vycor 791 has a guaranteed transmission of 70% at 254 m $\mu$ . for a 2-mm. thickness. In the infra-red the glasses have a sharp absorption band at 2.75  $\mu$ . The refractive index  $n_D$  is 1.458.

<sup>112</sup> *Glass Ind.*, 1944, 25, 399; C., 1945, 143.

<sup>113</sup> *Bull. Amer. Ceram. Soc.*, 1945, 24, 56; C., 1945, 145.

<sup>114</sup> *Elect. Rev.*, 1943, 132, 247.

<sup>115</sup> *J. Soc. Glass Tech.*, 1945, 29, 111; B., 1945, I, 389.



The optical properties of beryllium fluoride glass have been given by A. G. Pincus.<sup>116</sup>

The compositions of optical glass containing, in addition to the usual glass-making constituents, thorium oxide, tin oxide, and tantalum oxide, separately or together, have been disclosed in a Belgian patent granted to Schott u. Gen.<sup>117</sup>

The physical properties of the X-ray-transmitting beryllium-lithium-borate glasses and the limits of glass formation in the system have been given by L. Y. Mazelev.<sup>118</sup>

The compositions of two ultra-violet-transmitting glasses for bactericidal lamps have been given by V. P. Danilov and Z. A. Joffe.<sup>119</sup> The glasses contain no silica and have the compositions  $B_2O_3$  55,  $Al_2O_3$  17.5,  $BaO$  20.0, and  $Na_2O$  7.5% and  $B_2O_3$  60,  $Al_2O_3$  15,  $BaO$  25.0%. The glasses fuse at  $1150^\circ$  and are stated to devitrify more slowly than window glass made by the Fourcault process. They transmit light of wave-length  $254\text{ m}\mu$ .

A glass opaque to ultra-violet radiations shorter than  $280\text{ m}\mu$ , intended for use as an envelope of electric sun lamps, has been patented by H. Kalsing, H. Krefft, and K. Larche<sup>120</sup>; its composition is  $SiO_2$  72,  $K_2O$  11.5,  $Na_2O$  6,  $Al_2O_3$  0.5, and  $PbO$  10%.

An alumino-phosphate glass of high chemical stability and stated to be infra-red-absorbing has been described by N. B. Golubeva and I. M. Prok.<sup>121</sup> A patent on an alumino-phosphate glass for use as a base for colouring oxides has been granted to A. G. Pincus<sup>122</sup>; the specification covers glasses within the range of compositions  $P_2O_5$  45—80,  $Al_2O_3$  8—25, and  $SiO_2$  1—30%.

The subject of non-reflecting films continues to occupy the attentions of a large number of workers. R. L. Mooney<sup>123</sup> has given an exact theoretical treatment of reflexion-reducing coatings. Using Maxwell's electromagnetic equations, expressions are derived for the reflectivity and transmissivity of glasses with single homogeneous transparent films of uniform thickness and for two transparent homogeneous films of different thicknesses and refractive index. The conditions for minimum reflectivity are deduced. In a general article dealing with reflecting, non-reflecting, and reflecting-transmitting films, D. A. Lyon<sup>124</sup> has discussed their practical applications in optical elements.

As in previous years, a large number of patents on non-reflecting films and their method of application have appeared. G. L. Dimmick<sup>125</sup> has patented an improvement on the method of applying a mixture of

<sup>116</sup> *J. Opt. Soc. Amer.*, 1945, **35**, 92.

<sup>117</sup> Belg.P. 448,072.

<sup>118</sup> *Glass Ind.*, 1945, **26**, 373.

<sup>119</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 234; B., 1944, I, 101.

<sup>120</sup> U.S.P. 2,367,871.

<sup>121</sup> *J. Appl. Chem. Russ.*, 1944, **17**, 422; B., 1945, I, 330.

<sup>122</sup> U.S.P. 2,359,789.

<sup>123</sup> *J. Opt. Soc. Amer.*, 1945, **35**, 574.

<sup>124</sup> *Ibid.*, 157; C., 1945, 200.

<sup>125</sup> U.S.P. 2,371,611.



calcium fluoride and aluminium fluoride in which the mixed calcium and aluminium fluorides are evaporated in the proportions of their eutectic, a small amount of alumina being added to improve adhesion. Two other patents involving the evaporation product of mixed calcium and aluminium fluorides have appeared<sup>126</sup> and a patent on the application of metallic fluoride films has been granted to Kodak Ltd.<sup>127</sup>

As distinct from the methods of evaporating fluorides *in vacuo*, several patent specifications have appeared which make use of the leaching of alkalis from the glass surface, leaving a silica-rich layer. In two such patents,<sup>128,129</sup> the Radio Corporation of America employ the vapour from hydrofluoric or fluosilicic acids. F. W. Adams<sup>130</sup> treats the glass surface with 0.5N-nitric acid for 90 seconds followed by dilute hydrofluoric acid for 60 seconds. F. L. Jones and T. J. Zak<sup>131</sup> also employ the method of leaching out the alkalis.

The deposition of silicon compounds on the glass surface has been patented<sup>132</sup>; in this method, the surface is repeatedly wetted by a 1% solution of silicon bromide, chloride, or hydrochloride in a volatile non-aqueous solvent such as carbon tetrachloride. G. Weissenberg<sup>133</sup> deposits a silica layer by wetting the glass surface with an alkali silicate containing furfural, which is dried and then treated with hydrochloric acid to precipitate silicic acid; after washing and drying, a transparent silica coating remains.

C. W. Hansell<sup>134</sup> has proposed multiple coatings each 0.25 wave-length thick to obtain minimum reflexion over a wider wave-length band than is possible with a single coating. H. Osterberg<sup>135</sup> first deposits a transparent metallic coating of thickness not more than 0.1 wave-length; such a coating increases the reflexion from the surface but is covered with a non-metallic coating having an optical thickness of  $\frac{1}{8}$ — $\frac{3}{4}$  wave-length.

A method of testing the abrasability of non-reflecting films has been described by M. G. Townsley,<sup>136</sup> who suggests that the method is preferable to those which determine hardness in terms of resistance to indentation. Several methods of abrading the surfaces were tried and that finally adopted was a bundle of glass fibres reciprocated across the centre of a slowly rotated plane sample. The mechanical arrangement is such that the reciprocation gives a graded test, the results being assessed in

<sup>126</sup> Radio Corp. of America, B.P. 557,647; U.S.P. 2,372,639; B., 1944, I, 101.

<sup>127</sup> B.P. 558,867; B., 1944, I, 167.

<sup>128</sup> B.P. 558,098.

<sup>129</sup> B.P. 570,717.

<sup>130</sup> U.S.P. 2,348,704.

<sup>131</sup> U.S.P. 2,369,741.

<sup>132</sup> Pilkington Bros. and A. R. Wood, B.P. 569,857; B., 1945, I, 332.

<sup>133</sup> U.S.P. 2,356,553.

<sup>134</sup> U.S.P. 2,376,428.

<sup>135</sup> U.S.P. 2,366,687.

<sup>136</sup> *Rev. Sci. Instr.*, 1945, 16, 143; C., 1946, 128.



semi-quantitative terms. The method has proved useful in evaluating the effect of various procedures for producing more durable films.

### COLOURED GLASSES.

Two further sections of W. A. Weyl's monograph on coloured glasses have been published. The first section<sup>137</sup> deals with the colours produced by manganese, chromium, vanadium, copper, cobalt, nickel, uranium, titanium, tungsten, molybdenum, and oxides of the rare earth elements. The section includes a chapter on infra-red absorption and its effect on the melting and working properties of glasses. The second section<sup>138</sup> deals with colours imparted by the non-metallic elements sulphur, selenium, tellurium, phosphorus, and their compounds. Three short summaries of sections of Weyl's monograph have also appeared.<sup>139</sup>

V. Ctyroky<sup>140</sup> has published a report of an investigation of the effect of composition on the tint of glasses containing 1.5% of neodymium oxide; lead, barium, zinc, borosilicate, and lime base glasses were investigated. The zinc glasses were the most intensely coloured and the lime glass had the smallest effect. In the spectral range 400—600 m $\mu$ ., the absorption increased in the order lime, boric oxide, barium, lead, and zinc glasses. The effect of the addition of chromium oxide to a neodymium glass has been reported by V. Ctyroky and M. Fanderlik.<sup>141</sup> The addition of chromium shifts the colour of the neodymium glass towards the green, although the effect is small in glasses less than 5 mm. thick.

A coloured spectacle glass containing as colouring constituents 5—20% of Nd<sub>2</sub>O<sub>3</sub>, 0.5—1.5% of CuO, and 0.3—0.7% of Cr<sub>2</sub>O<sub>3</sub> has been patented by H. P. Hood.<sup>142</sup> The composition of a minus-green manganese-chromium filter glass with a low transmission for green light and a relatively high transmission for the remainder of the visible spectrum has been patented.<sup>143</sup> In the range of manganese content required to give the desired properties, the colour is difficult to control and the chromium oxide is added in the ratio of less than one part to 20 parts of manganese dioxide. An example of such a glass is SiO<sub>2</sub> 49, PbO 36, K<sub>2</sub>O 15, MnO<sub>2</sub> 0.08, and Cr<sub>2</sub>O<sub>3</sub> 0.002%.

A clear glass filter for use with a radiant energy source and transmitting 75% of the infra-red radiation and only 16—30% of the visible radiation has been patented<sup>144</sup>; this glass is a boron-free soda-lime-silica glass containing chromium, manganese, or selenium and cadmium. A patent

<sup>137</sup> *J. Soc. Glass Tech.*, 1944, **28**, 158; B., 1945, I, 127.

<sup>138</sup> *Ibid.*, 267; B., 1945, I, 224.

<sup>139</sup> N. I. Kreidl, *Glass Ind.*, 1944, **25**, 405; 1945, **26**, 235.

<sup>140</sup> *Sklarske Rozhledy*, 1943, **20**, 81.

<sup>141</sup> *Ibid.*, 121.

<sup>142</sup> U.S.P. 2,378,769.

<sup>143</sup> H. H. Blau, U.S.P. 2,357,994.

<sup>144</sup> T. W. Rolph and S. J. Harris, U.S.P. 2,360,280.



has been granted to M. E. Nordberg<sup>145</sup> covering the composition of a black glass suitable for glass fibres.

A novel method of producing a copper ruby glass has been patented.<sup>146</sup> The glass is fabricated in a colourless state from the melt containing a reducing agent and a copper compound and preferably stannic oxide. The article is irradiated by a mercury-vapour lamp and develops a blue colour which is changed to ruby on heating to the annealing temperature.

J. H. McLeod<sup>147</sup> has described a graphical method of correlating transmittances and thicknesses of optical filters. H. E. Powell<sup>148</sup> has suggested that McLeod's method of plotting can be modified to give a series of straight lines which converge at 92% transmittance and zero thickness. A method of controlling the thickness of sharp cut-off type filters has been described by H. P. Gage.<sup>149</sup>

#### NEW MANUFACTURING METHODS.

There is little to report on the subject of new methods of glass manufacture; as in previous years, practically all the novel information is in the patent literature.

F. Dumarest<sup>150</sup> has been granted a patent on a method of melting glass electrically. Three opposed pairs of electrodes are mounted horizontally through the side walls of a tank furnace and are movable in and out of the furnace. Current is fed to the electrodes from three independent similar circuits in such a way as to promote circulation in the tank by electrodynamic forces.

The manufacture of alkali silicates and glasses by the action of steam on silicic acid and an alkali chloride in the presence of an oxygen-containing acid or its anhydride or a salt of the acid has formed the subject of a patent<sup>151</sup>; it is stated that a vitreous mass is obtained if steam is allowed to react with a mixture of felspar and alkali chloride in the presence of boric acid.

A further patent on the method of manufacturing glasses of the Vycor type has been granted to M. E. Nordberg and H. E. Rumenapp.<sup>152</sup> In an earlier patent,<sup>153</sup> it was claimed that the introduction of aluminium nitrate prevented the development of opacity when a colorant was introduced into the glass; it is now claimed that the same result is achieved with compounds of phosphorus.

Another method of making multicellular glass in which the powdered glass is mixed with carbon and with the oxide of a metal having a volatilisation point below the temperature at which the glass fuses has been

<sup>145</sup> U.S.P. 2,353,354.

<sup>146</sup> B.P. 570,111; B., 1945, I, 332.

<sup>147</sup> *J. Opt. Soc. Amer.*, 1945, 35, 185; C., 1945, 200.

<sup>148</sup> *Ibid.*, 428; C., 1946, 55.

<sup>149</sup> *Ibid.*, 276.

<sup>150</sup> U.S.P. 2,350,734.

<sup>151</sup> Fr.P. 884,406.

<sup>152</sup> U.S.P. 2,355,746.

<sup>153</sup> U.S.P. 2,340,013B; .., 1946, I, 294.



patented by B. Long<sup>154</sup>; on heating the mixture, bubbles containing carbon dioxide and metal vapour are dispersed throughout the mass, which is cooled to form multicellular glass. The methods of making multicellular glass have been reviewed.<sup>155</sup>

Three patents on processes dealing with glass fibres are due to G. von Pazsiczky. In the first of these,<sup>156</sup> the molten glass is fed into a vessel rotated at high speed and by centrifugal force is thrown through orifices in the wall of the vessel. In the second patent<sup>157</sup> small amounts of glass of thermal expansion characteristics different from those of the main glass are introduced for the purpose of producing curled fibres. The third patent<sup>158</sup> covers a method of roughening the surface of glass fibres either by introducing hydrofluoric acid vapour into the blast employed for attenuating the fibres or by passing continuously produced fibres through a chamber containing stannic chloride vapour.

#### MISCELLANEOUS.

In discussing the physical and chemical properties of Vycor, M. E. Nordberg<sup>25</sup> has given some properties of the intermediate stage of porous glass. The void space is estimated to be 28% of the volume with an average pore radius of 28 Å. Data are given on the shrinkage of the porous glass with time at various temperatures. For each temperature there is a definite amount of shrinkage, but complete consolidation takes place at 1200°, when the glass shrinks to 65% of its original volume. The flow of liquids through the porous material was found to be proportional to the applied pressure and inversely proportional to the thickness and to the viscosity of the liquids.

S. R. Scholes<sup>159</sup> has studied the abrasability of glass of various compositions, values being obtained by grinding on a steel plate with powdered quartz as the abrasive. The results were compared with those obtained on silica rods. Although no particular degree of hardness could be attributed to the individual components of the various glasses, it was found that silica and boric oxide contributed most to the abrasion-resistance while soda, lime, and lead produced high abrasability. Commercial glasses showed no great range of abrasability but were approximately three times as abrasable as pure silica with the quartz abrasive used. With silicon carbide there was little difference between glass and silica.

An analysis of various types of fracture encountered in glass, in which the fracture patterns are correlated with the stress conditions, has been described by C. D. Oughton.<sup>160</sup> A study of the "rib" marks and

<sup>154</sup> U.S.P. 2,337,672; B., 1946, I, 275.

<sup>155</sup> *Ceram. Ind.*, 1944, 42, 47.

<sup>156</sup> U.S.P. 2,338,473.

<sup>157</sup> U.S.P. 2,331,945.

<sup>158</sup> G. von Pazsiczky and H. Steingraber, U.S.P. 2,331,944.

<sup>159</sup> *J. Amer. Ceram. Soc.*, 1945, 28, 133; B., 1945, I, 293.

<sup>160</sup> *Glass Ind.*, 1945, 26, 72; B., 1945, I, 331.



"hackle" marks on fractured surfaces described by F. W. Preston<sup>161</sup> furnishes a considerable amount of information concerning fractures and it is possible to determine (1) the origin of the fracture, (2) the direction of travel, (3) regions of tension and compression at the time of fracture, (4) whether explosive or slow travelling, (5) strain condition of the glass, (6) whether shock is mechanical or thermal, (7) whether mechanical shock is a severe blow or a steady force. Fractures initiated under particular conditions are illustrated by photographs.

R. F. Scott<sup>162</sup> has studied the type of fracture produced by impact in laminated glass consisting of two discs  $\frac{1}{16}$  in. thick cemented together with plastic bond. Three distinct types of fracture were observed, namely, an impact cone, radial fractures on both upper and lower discs, and spiral fractures which appeared only in the impacted glass. The first two types of fracture are well known and the spiral fracture is attributed to a shift of the original compression stress in the impacted surface to a tension as the glass rebounds after impact.

Several papers have been published during the course of the year on the subject of glass-metal seals. A note on the properties of glasses for sealing to metals and metal alloys has been published<sup>163</sup> and G. D. Redston and J. E. Stanworth<sup>164</sup> have described an experimental investigation in which the stresses in such seals were measured over a wide range of temperature and the stress was related to thermal expansions, elasticities, and relaxation properties of the materials used. Between room temperature and the annealing range the stress varied considerably and at any temperature could be altered by variation in the thermal treatment of the seal. In the annealing range the stress was modified by viscous flow. Stresses in bead seals were investigated and the mathematical accuracy of the Hull-Burger equations was confirmed. In bead seals, the measurement of the axial stress is taken to be indicative of the probable behaviour of a bead seal and also for a rapid control method for checks on the thermal expansion of the glasses used. R. W. Douglas<sup>165</sup> has discussed glass-metal seals, particularly those used for lead-in seals in vacuum devices. He points out that the stress in the seal is dependent on the thermal history of the seal and describes methods of devising heat-treatments which minimise the stresses in particular cases. A. E. Dale and J. E. Stanworth<sup>166</sup> have described the properties of various sealing glasses, both for intermediates between glasses and for sealing to metals. A nickel-chromium-iron alloy suitable for sealing to Corning glasses G.1 and G.12 has been described in the patent literature.<sup>167</sup>

<sup>161</sup> *J. Soc. Glass Tech.*, 1926, 10, 234r.

<sup>162</sup> *Glass Ind.*, 1945, 28, 181.

<sup>163</sup> *J. Sci. Instr.*, 1945, 22, 38.

<sup>164</sup> *J. Soc. Glass Tech.*, 1945, 29, 48r; B., 1945, I, 389.

<sup>165</sup> *Ibid.*, 92r; B., 1945, I, 389.

<sup>166</sup> *Ibid.*, 77r; B., 1945, I, 389.

<sup>167</sup> W. E. Kingston, U.S.P. 2,371,627.



R. W. Douglas<sup>168</sup> has surveyed the uses of glass in high-vacuum apparatus and the essential properties of such glasses are discussed.

E. C. Marboe and W. A. Weyl<sup>169</sup> have described a new method for the chemical deposition of copper mirrors on to glass in which the glass surface is modified to permit the deposition of the copper. The copper is deposited from copper tartrate-formaldehyde solution on to a silver surface which has been deposited on the glass, the thickness of the silver being insufficient to contribute to light absorption on reflexion. The silver ions are deposited by a base exchange with the univalent alkali ions present in the glass. Such a reaction does not occur with cupric ions, so that the deposition of the silver enables a copper mirror to be formed.

Two patents concerned with the etching of glass have been granted to F. W. Adams. According to the first patent<sup>170</sup> the glass surface is coated with a continuous liquid film consisting of a suspension in a volatile non-solvent medium of fine organic plastic particles which are resistant to the etching acid; the medium evaporates, leaving the particles distributed on the glass surface, thus providing dispersed points of protection when the glass is etched. In the second patent<sup>171</sup> the liquid film contains, in addition to the plastic, dispersed particles of inorganic pigment. Adams has also patented a method of polishing glass surfaces, applicable particularly to soda-lime-silica glass<sup>172</sup>; the method consists of subjecting the glass to the frictional action of a suspension of rouge in a dilute halogen acid containing a soluble alkali-metal salt. It is claimed that the method speeds up the polishing process.

T. J. Thompson<sup>173</sup> has discussed the uses of glass in engineering. New forms of glass such as fibre glass and the manufacture of complex glass equipment for chemical apparatus by electric welding are finding increasing application. Thompson also mentions precision bore glass tubing with inside diameters accurate to  $\pm 0.0004$  in.; a description of such tubing has been given elsewhere.<sup>174</sup> The uses of glass in chemical engineering have been reviewed by J. H. Koffolt and J. R. Withrow.<sup>175</sup>

A patent in the composition of a glass for fibres has been granted to W. Eitel and A. Dietzel.<sup>176</sup> The glass contains thoria and zirconia in addition to silica, alumina and titania, *e.g.*, SiO<sub>2</sub> 60, Al<sub>2</sub>O<sub>3</sub> 5, TiO<sub>2</sub> 10, ZrO<sub>2</sub> 10, Na<sub>2</sub>O 15%.

M. B. Vilensky has been granted two patents on platinum alloys suitable for glass feeders. The first patent<sup>177</sup> covers alloys falling within

<sup>168</sup> *J. Sci. Instr.*, 1945, **22**, 81; C., 1945, 217.

<sup>169</sup> *Glass Ind.*, 1945, **26**, 119; B., 1945, I, 331.

<sup>170</sup> U.S.P. 2,359,071.

<sup>171</sup> U.S.P. 2,359,072.

<sup>172</sup> U.S.P. 2,366,825.

<sup>173</sup> *Met. and Alloys*, 1945, **21**, 94.

<sup>174</sup> *J. Sci. Instr.*, 1945, **22**, 116.

<sup>175</sup> *Ohio State Univ. Eng. Expt. Sta. News*, 1944, **16**, 13.

<sup>176</sup> G.P. 727,779.

<sup>177</sup> U.S.P. 2,188,636; B., 1945, I, 136.



the range of compositions Pt 90—98, Ir 1.5—8, and Ni 0.3—2%; the compositions covered by the second specification<sup>178</sup> are within the range Pt 98—99.75% and Ni 0.25—2%. A patent has appeared on a method of moulding glass which consists of mixing finely powdered glass with an organic binder and an oxidising agent and firing to within 25° of the softening point after moulding to form a glassy structure.<sup>179</sup>

R. F. Baker and F. H. Nicoll<sup>180</sup> have investigated the silica replica method of surface examination for use with the electron microscope; the silica replica is obtained by chemical decomposition of silicon tetrachloride. In testing the method, replicas of frosted glass and of non-reflecting film on window glass were examined and photographs ( $\times 31,500$ ) are included in the paper.

<sup>178</sup> U.S.P. 2,361,578.

<sup>179</sup> B.P. 567,996; B., 1945, I, 187.

<sup>180</sup> *J. Appl. Physics*, 1944, 15, 803; A., 1945, I, 192.



# CERAMICS, REFRACTORIES, AND CEMENTS.

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THE end of hostilities has resulted in an immediate increase in research publication, and its subject matter gives some indication of the lines on which the industry has been thinking in war-time. It is apparent that much development has taken place in the design of tunnel kilns used for continuous firing, with a tendency towards types of smaller cross-section than usual. The substitution of the standard wet mixing process by dry mixing with specially prepared raw materials has made progress in those sections of the ceramic industry making dust pressed goods. In the tableware section automatic making and even mechanised decorative processes are making headway.<sup>1</sup> The export value of British tableware lies more in its quality than its price, and it is a matter of some concern to avoid lowering quality by the introduction of mechanisation.

Accumulated experience on various special types of refractories shows the extent to which their use has developed under conditions of high output.

The iron enamel division still appears to lack research development in this country, although this does not necessarily mean that modernisation of existing industry is not taking place, but there are grounds for the belief that this section of the ceramic industry is lagging behind some of its international competitors so far as research is concerned. The cement industry appears to be in a somewhat similar relative position.

## CLAYS AND OTHER RAW MATERIALS.

Several important papers on the fundamental properties of ball clays have appeared in the period under review. Base-exchange phenomena in clays and ceramic materials have been reviewed<sup>2</sup> and the total exchange capacity of a large number of typical English ball clays has been determined. It is characteristic of English ball clays that they are unsaturated with regard to metallic ions (though this is not true of some of the selenitic and dolomitic red burning clays used for building materials).  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions are readily and completely removable from clays, but  $\text{Na}^+$  and  $\text{K}^+$  ions appear to be progressively removable, suggesting that some of them are below the surface of the clay particle.<sup>3</sup> It is sometimes overlooked, however, that much of the feldspar content of such clays

<sup>1</sup> H. F. Allen, *Ceram. Age*, 1945, **45**, 46. W. J. Miller, U.S.P. 2,370,410. W. H. Glenn, U.S.P. 2,373,468.

<sup>2</sup> D. A. Holdridge and M. Francis, *Trans. Ceram. Soc.*, 1944, **43**, 131; B., 1945, I, 65.

<sup>3</sup> Cf. C. E. Marshall, *ibid.*, 1931, **30**, 81; 1936, **35**, 401.



is of a grain size well below the colloid limit and such particles are progressively decomposed by water and aqueous solutions. A much wider study of the fundamental properties of clays which influence their use,<sup>4</sup> such as base-exchange capacity, heat of wetting, pH, equilibrium water content, permeability, porosity, rate of drying, and dry strength, has confirmed the importance of base-exchange capacity in relation to all these properties. A number of single-base clays were compared and evidence was obtained that the pore structure and volume have a direct influence on factors such as permeability, drying rate, and dry strength, but it is probable that both pore structure and volume are determined to a considerable extent by the character of the cation attached to the clay. For example, when the adsorbed ion is  $\text{Na}^+$  the clays have a dense stable pore structure causing bad drying characteristics, high dry strength, and low permeability, while the action of the  $\text{H}^+$  ion is the reverse of this. Incidentally, the behaviour of carbonaceous clays is anomalous, a result which the authors suggest is due to the presence of organic ions. It may well be due to the action of a protective colloid, however. The importance of the degree of hydration of the cation does not seem to have been fully appreciated. In this connexion R. E. Grim and F. L. Cuthbert<sup>5</sup> have shown (on certain assumptions) that the water layers on  $\text{Na}^+$ - and  $\text{Ca}^{++}$ -montmorillonite clay particles are 3 and 4 molecules thick respectively. They also show that with some clays, e.g., kaolinite and halloysite, the adsorption of water is not completed rapidly and the "workability" of the clay changes with time, a fact which is of practical importance in relation to the method of dry mixing now being adopted in some sections of the industry.

A useful summary of factors which influence the strength of clay ware has been published.<sup>6</sup> The term mechanical strength is often used loosely without sufficient indication of whether it is tensile or compressive strength or resistance to abrasion which is meant. Some factors affect the tensile strength in an opposite way to their effect on the crushing strength. A point often overlooked is that the method of making the clay ware has a direct effect on the tensile strength both fired and unfired. Slip casting, plastic making, and dust pressing all give appreciable differences with the same body. It is not a question of pore volume, since the plastic-made body with the highest porosity in the unfired state has the lowest porosity in the fired state and also the greatest tensile strength in both circumstances.

The internal stresses of ceramic bodies which arise from expansion differences in a heterogeneous grain structure need investigation. There is evidence that most table-ware, certainly earthenware, has considerable internal stresses apart from those due to the relative expansion coefficients

<sup>4</sup> C. G. Harman and C. W. Parmelee, *J. Amer. Ceram. Soc.*, 1945, **28**, 110; B., 1945, I, 257.

<sup>5</sup> *Ibid.*, 90; B., 1945, I, 186.

<sup>6</sup> H. W. Webb, *Chem. and Ind.*, 1945, 178; B., 1945, I, 257.



of glaze and body. Data on the compressibility of a large number of British and foreign clays have been reported.<sup>7</sup> The highly colloidal clays are more compressible and show greater void ratios than sandy clays under a given pressure.

A detailed examination of a large number of U.S.A. talcs for possible use in high-frequency insulator bodies is of general interest to the industry.<sup>8</sup> Some work on the effect of variation in grain size of talc from commercial supplies on vitrification in talc-ball clay compositions<sup>9</sup> shows that its behaviour is rather like that of Cornish stone and felspar in earthenware bodies, in that appreciable differences in fineness have relatively little effect on firing shrinkage. This appears to be generally true of ceramic fluxes, the grain size of the accompanying refractory constituents (*e.g.*, flint) having a much greater influence on vitrification than the grain size of the flux itself.

Two applications of flotation processes for the purification of ceramic materials are of interest.<sup>10</sup> In one case the process was examined for the removal of quartz from a high-silica kaolinite and in the other for the removal of the iron-bearing constituent of pegmatite. The methods were practicable but are very unlikely to be economic.

Organic binders are used in various sections of the ceramic industry. For example in the fireclay sanitary industry the glaze is set by gelatin to a jelly-like consistency in order that it may be applied by brushing. Gums and waxes are frequently added to glaze suspensions in order to get better glaze adhesion before firing, and so avoid loss through particles of dried glaze falling off when placing in the kiln. The efficacy of the various substances available for use as binders varies very much. Some recent work on comparative binding powers of various organic materials<sup>11</sup> using ground flint as a test material showed that gelatin, casein, and peptone were the best, while substances such as dextrin, cornflour, and wax emulsion were much less efficient, giving only about one tenth the adhesive power. It is perhaps unfortunate that a number of the newer synthetic resin adhesives were not included for comparison, since some of them are many times as effective as the best natural organic binder.

#### CERAMIC BODIES AND MAKING PROCESSES.

The extent of mechanisation in pottery production is not easily deducible from research publications. Before this war the application of engineering methods to the industry made little progress for a number

<sup>7</sup> A. W. Skempton, *Quart. J. Geol. Soc.*, 1944, **100**, 119; B., 1945, I, 68.

<sup>8</sup> T. A. Klinefelter, S. Speil, and S. Gottlieb, *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3804; B., 1945, I, 258.

<sup>9</sup> J. S. White, *J. Amer. Ceram. Soc.*, 1944, **27**, 320; B., 1945, I, 66. Cf. R. S. Lamer, *ibid.*, 317; B., 1945, I, 66.

<sup>10</sup> H. H. Kellogg, *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1753; B., 1945, I, 154. W. Theilheimer and H. Erlenmeyer, *Helv. Chim. Acta*, 1944, **27**, 1428; B., 1945, I, 100.

<sup>11</sup> E. P. McNamara and J. E. Comeforo, *J. Amer. Ceram. Soc.*, 1945, **28**, 25; B., 1945, I, 135.



of years, and while in U.S.A. it has made tremendous strides in recent years, that is not true of the home industry. Some of the figures appertaining to the American position are very striking.<sup>12</sup> Three automatic making machines at one plant for example are producing 46,000 dozen pieces per day, which is nearly the weekly production of one of the larger British potteries. The number of workers required in the production of the unfired clay article is reduced to nearly one tenth in the mechanical process as compared with the usual type. Such a mechanised procedure would be undesirable in a pottery aiming at high-quality ware in reasonable variety, of course, but the industry may have the problem of trying to run the two types of production side by side.

Mechanisation in electrical porcelain and special ceramic radio components has also made considerable strides. Certain types of production are now dealt with on automatic lathes and indeed there are items which are handled entirely on a line production system very similar to the standard engineering assembly. Products made by dust pressing have been easier to produce on a mechanised basis than plastic-made materials, and this section of the industry is well in advance of others on the mechanical side of its equipment.

Experience in the use of infra-red drying units has now been obtained by a number of potteries both in U.S.A. and in this country.<sup>13</sup> The limitations of the method are now more clearly realised. As would be expected, drying at high speeds is much easier with ceramic bodies of low drying-shrinkage, *i.e.*, those with the least plastic clay content as a rule. In the case of flat ware which has to be dried while resting on a plaster mould the great difficulty is that of distortion. Some potteries have tried to solve this by using a low-intensity source of radiation such as filament lamps to dry the ware just enough to enable it to be released from the mould. The additional handling of ware in a fragile state involved by this procedure is not very satisfactory, however. High-intensity radiation drying is not really suitable for clay articles of any thickness and it is possible that the problem of high-speed drying would best be solved by a combination of infra-red radiation and convection drying. A rapid system of obtaining the release of cups etc. from the plaster moulds in which they are made, preparatory to fixing on the handle, is by blowing a jet of warm air directly into the ware while in the mould. A dryer has been patented<sup>14</sup> in which the goods are carried on rotating shelves with a downward jet of air blowing into the ware. The air ducts are hollow shelves and are perforated to form jets in register with the ware. In this way the moulds are brought back to the maker.

A drying method of limited application<sup>15</sup> covers the moulding of

<sup>12</sup> W. J. Miller, *Ceram. Age*, 1944, 44, 104.

<sup>13</sup> R. E. Gould, B. B. Evans, and A. M. Flannigan, *Bull. Amer. Ceram. Soc.*, 1945, 24, 62; B., 1945, I, 187. R. N. Green, *ibid.*, 8; B., 1945, I, 187.

<sup>14</sup> Swinnertons Ltd., and R. B. Bloore, B.P. 565,989; B., 1945, I, 101.

<sup>15</sup> D. W. Ross, U.S.P. 2,320,474; B., 1945, I, 127.



ceramic articles to shape on an electric conductor having low-resistance leads. The article is surrounded by a removable porous mass or support and is dried by the heating effect of the current and a certain amount of electro-osmosis. A theoretical and experimental study of (hot-floor) drying based on data obtained from a laboratory-scale apparatus<sup>16</sup> gives some interesting relationships between the rates of drying under conditions in which the rate of air circulation is varied and in which the ware is preheated before submitting it to drying conditions. The introduction of an artificial plasticity or workability in ceramic articles has been tried very frequently and with indifferent success so far. If the necessity for the use of clay to give the mouldability and tensile strength (unfired) can be obviated, very different drying and firing cycles are possible. The use of 1—2% of a cellulose ether capable of swelling or dissolving in water has recently been claimed for this purpose.<sup>17</sup> Increase of plasticity in clay bodies is also claimed from the addition of a primary alkylamine (alkyl not higher than C<sub>10</sub>) or a salt thereof,<sup>18</sup> whilst the use of a hydrous zeolite gel is also suggested.<sup>19</sup>

#### GLAZES AND COLOURS.

The solvent action of a glaze, when molten, on the surface of the underlying biscuit ware has always been assumed to be an important factor in aiding crazing-resistance, quite apart from the relative expansion coefficients of glaze and body. It is not easily possible to prove the effect of this interpenetration on crazing-resistance, however, since by penetration the composition of the glaze layer is changed and it becomes more refractory and of lower expansion coefficient. Furthermore the variation in glaze thickness which arises through penetration also has a direct effect on crazing-resistance. By compounding the same glaze in a number of different ways so that the fritted portion melts at a different time in the firing, it is possible to demonstrate that the crazing-resistance varies widely with the melting temperature of the fritted part, being the greater, in general, the lower is the melting temperature. Since the ultimate composition of the glaze is the same, it can be assumed that the increased crazing-resistance is due to the earlier attack and penetration by the softer frit, on the biscuit ware. The formation of this "buffer layer" is a well-known phenomenon, of course. It is also a matter of experience that once-fired ware (which is glazed in the clay state) is more crazing-resistant than twice-fired ware, and although no definite proof is available, it has been assumed that the greater crazing-resistance is due in part to the greater penetration of the clay by the glaze, since once-fired ware has longer periods of firing and at a higher temperature as a rule than ordinary glost ware. Some recent work on

<sup>16</sup> H. H. Macey and F. G. Wilde, *Trans. Ceram. Soc.*, 1944, 43, 93; B., 1944, I, 366.

<sup>17</sup> W. L. C. van Zwet, U.S.P. 2,322,179; B., 1945, I, 188.

<sup>18</sup> A. W. Ralston and E. J. Hoffmann, U.S.P. 2,320,009; B., 1945, I, 156.

<sup>19</sup> W. K. Carter, U.S.P. 2,318,753; B., 1945, I, 101.



these points,<sup>20</sup> in which the extent of glaze penetration was roughly measured, showed that where the glaze penetration was greater, the glazed body showed a higher crazing-resistance as measured by the degree of compression of the glaze, and it was possible to get crazing-resistance at a lower total flint content of the body than normal by using a glaze of high penetrating quality. It is obvious, of course, that the weakness of the data lies in the fact that a change in glaze composition to alter its penetration causes a change in its intrinsic expansion coefficient, and in the case of  $B_2O_3$  variation this is not a straight-line effect.

The glaze pick-up obtained by dipping a porous body into a glaze slip is known to vary with the porosity of the ware, time of immersion, ratio of solids to water in the slip, the fineness of suspended glaze, and the viscosity of the glaze slip. The last-named is by far the most important factor. In the dipping of vitreous bodies another factor comes into the picture, which has been called the coherence value or cohesive value, and is of great importance in iron enamelling. It can best be demonstrated by the immersion of a smooth glass plate in the glaze slip and measuring the amount of glaze adhering after the vertical withdrawal of the plate. Generally speaking this quantity increases with increasing viscosity of the suspension up to a critical point when the glaze slip is too thick to wet the glass surface properly. A detailed study of some of these factors is of interest.<sup>21</sup> The empirical relationship is put forward for calculating the glaze pick-up,  $P = (KR/100)(C - 0.001)$ , where  $C$  = cohesive value in g. per cm.<sup>2</sup>,  $R$  = water receptivity, which is the amount of water absorbed per 1 sq. cm. area of body when immersed in water for 5 seconds,  $K$  is a deposition constant which varies for different glazes, and  $P$  = glaze pick-up. The values of  $K$  vary widely; e.g., for a raw feldspathic type glaze  $K = 4.34$ , for a raw lead glaze 1.8, and for a fritted glaze 3.26.

Similar considerations have been applied to clay slips where the colloid content is, of course, much higher, and indications are that the cohesive value is related to the base-exchange capacity of the clay. An account of the theory and practice of coloration in silicates is of general interest.<sup>22</sup> This is a continuation of some work which has already been published.<sup>23</sup> The influence of ionisation needs further study and also the effect of dispersion in the silicate melt, a factor which greatly influences the colouring effect of gold, for example. A revival of interest in the manufacture of cooking ware using vitreous bodies of very low expansion has aroused a corresponding interest in the search for low-expansion glazes which will fit these bodies without crazing. It is true in a broad sense that the higher is the softening temperature of a glaze the lower is its

<sup>20</sup> E. Thomas, M. A. Tuttle, and E. Miller, *J. Amer. Ceram. Soc.*, 1945, 28, 54; B., 1945, I, 186.

<sup>21</sup> C. G. Harman and H. C. Johnson, *ibid.*, 1944, 27, 202; B., 1945, I, 25.

<sup>22</sup> W. A. Weyl, *J. Soc. Glass Tech.*, 1944, 28, 158t, 267t; B., 1945, I, 127, 224.

<sup>23</sup> W. A. Weyl, *ibid.*, 1943, 27, 133t; B., 1944, I, 136.



coefficient of expansion, so that while it is possible to produce low-expansion bodies maturing at a temperature range of say 1200—1300°, it is not apparently possible to compound a glaze of still lower expansion which will mature within the same (or a lower) temperature range. The term "low-expansion" in reference to a cooking ware body is, of course, a relative term. A coefficient of  $4.0 \times 10^{-6}$  is low in comparison with that of the usual earthenware and stoneware bodies sold as oven ware, but it is very difficult to compound a glaze which will mature at say 1250° with an expansion coefficient lower than this, or even equal to it. The glaze described by J. Marquis<sup>24</sup> as a low-expansion glaze, for example, would have an expansion coefficient very much greater than this. A closer approach to the expansion coefficients which may ultimately be required for a successful solution is by the use of pre-melted low-expansion glass, but the melting temperatures of such glasses are very high. For example, a glass with a thermal expansion of  $0.8 - 1.5 \times 10^{-6}$  is founded at 2000°, and a great proportion of the necessary heat for doing this is obtained by the passage of current through the glass.<sup>25</sup> C. G. Harman<sup>26</sup> calls attention to the well-known fact that a crystalline glaze has a much greater crazing-resistance, *cæteris paribus*, than a bright glaze, and suggests that the problem of glaze fit on low-expansion bodies might be solved by using a glaze which will crystallise. Some further work involving, amongst other factors studied, the effect of lithium oxide, strontium oxide, and nepheline syenite in leadless glazes,<sup>27</sup> suggests that no benefits are obtainable by the substitution of  $\text{Li}_2\text{O}$  for  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ , a point about which many varying claims have been made in the past. In addition,  $\text{SrO}$  is preferred to  $\text{BaO}$ , because while increasing the fusibility at least as much as  $\text{BaO}$ , it is claimed that it does not increase the expansion coefficient so much and is hence a help to crazing-resistance without loss of flow in the molten glaze. Incidentally the effect of such oxides as  $\text{BaO}$  and  $\text{SrO}$  on underglaze colours is often overlooked, when findings are merely concerned with melting points and expansion coefficients. The importance of fine grinding on the dissolution of quartz in the glaze is emphasised, but it is well-known, of course, that different forms of silica have a very different rate of dissolution in a glaze and with some of them it is possible to grind relatively coarsely (with saving in grinding cost) and still obtain complete melting.

Some further work on the fluxing effect of  $\text{SrO}$  in borosilicate glasses<sup>28</sup> shows that  $\text{SrO}$  is a stronger flux than either  $\text{BaO}$  or  $\text{PbO}$  in glasses high in  $\text{CaF}_2$  and low in  $\text{Al}_2\text{O}_3$ . The button flow method which the authors used is greatly influenced by the viscosity of the melt apart from its softening point, and conclusions about fluxing power based on

<sup>24</sup> *J. Amer. Ceram. Soc.*, 1944, 27, 358; B., 1945, I, 127.

<sup>25</sup> General Electric Co., Ltd., and J. H. Partridge, B.P. 568,469; B., 1945, I, 258.

<sup>26</sup> *J. Amer. Ceram. Soc.*, 1944, 27, 231; B., 1944, I, 400.

<sup>27</sup> C. G. Harman and H. R. Swift, *ibid.*, 1945, 28, 48, 52; B., 1945, I, 185.

<sup>28</sup> H. R. Swift, *ibid.*, 33; B., 1945, I, 185.



this test alone are unreliable. Some of these findings are improbable on a physico-chemical basis. E. S. McCutchen,<sup>29</sup> for example, finds that the substitution of PbO in a glaze by SrO raised the softening temperature and increased the viscosity of the melt and also the thermal expansion. The substitution was made on a molar basis (as it should be) and confusion sometimes arises when the substitution is made on a weight for weight basis. This work suggested that the most fruitful field for the use of SrO lay in leadless glazes. It is well-known that salt glazing is not practicable with ware which is not near complete vitrification when the salt vapour is applied. An interesting method of vapour-glazing ware (*e.g.*, bricks) which are not fired to complete vitrification has been described.<sup>30</sup> In order to obtain a vitreous surface the ware is sprayed before firing with an engobe which will vitrify at the maturing temperature of the ware. A spray of zinc chloride is then applied and salt is volatilised into the kiln during firing in the ordinary way.

An important piece of fundamental work on the surface tension of glazes may enable the prediction to be made of the tendency of a glaze to show such faults of crawling and ruckling and so on.<sup>31</sup> Surface tension appears to be an additive property, and new molecular factors derived for a range of oxides are given to calculate surface tension within reasonable limits of accuracy. The influence of surface tension in the maturing of a glaze is of considerable importance, and it will be of great help if the change in surface tension (even if only relative) with change in glaze composition can be calculated with reasonable certainty.

### ENAMELS.

The general trend of the industry over the war period has probably been towards lower maturing temperatures (especially in ground-coat enamels to mature at the same temperature as the cover coats), lighter application weights with no loss of reflectance, and in the development of acid-resistance. The change from the use of antimony-containing opacifiers to those containing zirconium compounds has been necessitated by war-time restrictions, but undoubtedly some of the zirconium compositions will hold their place in the post-war market, especially for acid-resisting types. The production of an enamelling iron to which white finish coat enamels could be applied directly without the use of a ground coat has attracted a good deal of research interest, involving amongst other things the problem of adherence and special methods of treating the surface to enhance this. The possibility of applying finished coat enamels directly to the metal is well within sight and may mean the elimination of a large number of ground-coat enamels now in use. Methods of pickling are always the subject of change, but the molten salts bath (Kolene) and "gas pickling" are two of the more recent types under

<sup>29</sup> *Ibid.*, 1944, 27, 233; B., 1944, I, 399.

<sup>30</sup> W. S. Ramsay and G. A. Bole, U.S.P. 2,320,099; B., 1945, I, 129.

<sup>31</sup> K. C. Lyon, *J. Amer. Ceram. Soc.*, 1944, 27, 186; B., 1944, I, 334.



investigation which may entirely alter normal pickling methods. In both cases cleaners and acids might be made unnecessary.

Automatic spraying is also being developed, and in this connexion the use of an electrostatic field in the spraying booth is an interesting possibility. With competition from the light alloy industry rapidly increasing, it is to be expected that the standards of production and service specifications for enamel ware will attract constant attention, and the holloware producers particularly are aiming at high specification standards. The problem of enamel adherence is one of the most important. The testing of enamel adherence by the usual impact test is subject to a number of errors, as is well known. The thickness of metal, thickness of enamel, and radius (in the case of curved vessels) all affect the result. Generally speaking impact-resistance increases with thickness of metal and of enamel coating. It is also greater the lower is the radius of curvature of the surface.<sup>32</sup> The effect of curvature follows from the mechanics of a surface layer under compression, but should vary theoretically with the shape of the surface, *i.e.*, whether concave or convex, and a different value would be expected for the inside as compared with the outside of a curved vessel. In this connexion a modified form of impact test has been tried in which observations on damage to the enamel are made on the opposite side of the place where the impact occurs. Some observations on the effect of surface condition on enamel adherence have been made using an impact test of this type.<sup>33</sup> In particular the adherence of grip coats was examined, without a cover coat being applied. The adherence depends to a large extent on the roughness of the metal surface before enamelling. The use of restrainers to prevent excessive acid attack during pickling does not appear to favour enamel adherence. Cold hydrochloric acid is not so favourable as hot sulphuric acid. Sulphide pickling with hot sulphuric acid appears to be most effective as a surface roughener, and it does not matter whether hydrogen sulphide is bubbled into the vat or ferrous sulphide added. At one time there was a good deal of interest in sand blasting as a surface treatment, and the process is still used as it gives better adherence than pickling. It is more liable to produce enamel defects through imperfect cleaning, however. Electrolytic pickling is also rather out of favour. The cathodic process is good for cleaning the metal, but is thought to increase faults arising from occluded hydrogen. Anodic etching is satisfactory except for equipment. Claims made at one time of the value of manganese dioxide in assisting enamel adherence do not appear to be justified.<sup>34</sup> The solution of the problem of adherence is closely bound up with the practicability of one-coat enamels of good quality. In this connexion the use of an iron-eroding paste containing sodium antimonate as an (unfired) pre-coating for the metal, prior to spraying

<sup>32</sup> F. A. Petersen and A. I. Andrews, *ibid.*, 1945, 28, 102; B., 1945, I, 257.

<sup>33</sup> *Ann. Proc. Inst. Vitreous Enamellers*, 1941-2, 7, 40; B., 1945, I, 155.

<sup>34</sup> R. M. King, *J. Amer. Ceram. Soc.*, 1944, 27, 350; B., 1945, I, 65.



with a cadmium sulphoselenide enamel and firing, is of some interest.<sup>35</sup> During the war years there has been some development in electrostatic spraying, that is, the use of a high-voltage field around the article being sprayed. The process has been used successfully in the paint industry, but so far the application to enamels has been only experimental.<sup>36</sup>

### REFRACTORIES.

There are many interesting examples now available of the results of experimental work on the use of special refractories for special jobs. The use of different forms of carbon brick linings in blast-furnace work is a case in point. The results have been so promising that carbon may replace a good deal of firebrick for this purpose. The advantages claimed for the material are that it is in chemical equilibrium with the molten iron (which is saturated with carbon); it has no contraction at normal working temperatures; its thermal expansion is not high; it is light and easily mouldable into larger blocks than is possible with other types of material, so reducing the number of joints, and it can also be rammed and burned to form a monolithic lining. There are many other similar examples. The action of copper-reverberatory slag on magnesite, chromite, forsterite, and fireclay bricks for instance<sup>37</sup> shows the relative value of magnesite and chromite for this type of furnace, and a closely packed mixture of coarse chromite and fine magnesite grains is recommended. The use of basic linings in copper-reverberatory furnaces is not new, of course, but is recent in development. For the tuyère zone of converters magnesite is now the most widely used lining, whilst for various refining operations, chemically bonded basic bricks are replacing silica bricks.<sup>38</sup> The value of zircon refractories in aluminium smelting furnaces is stressed by R. W. Knauf.<sup>39</sup> Zircon bricks are not wetted by molten aluminium or alumina-aluminium mixtures, nor do they suffer alteration like firebricks through a thermit reaction. They are also resistant to spalling and do not contaminate the metal, an important factor in this case. Zircon refractories are also promising in phosphate (especially metaphosphate) production. Although the furnace temperature is not high (below 820°), resistance to phosphate corrosion at this temperature is very difficult, and zircon is offering promise of greatly increased life because of its high resistance to phosphate attack. Zircon bricks may be bonded with water-soluble phosphates with success. A dry, ready-mixed composition for this purpose, which requires only the addition of water, consists of a mixture of zircon and a small amount of a non-deliquescent acid ammonium phosphate, or of an inorganic or organic derivative of ammonia. The solubility of the phosphate must

<sup>35</sup> J. E. Rosenberg, Assr. to Homelaya Inc., U.S.P. 2,317,114; B., 1945, I, 225.

<sup>36</sup> J. B. Willis, *J. Amer. Ceram. Soc.*, 1945, 28, 121; B., 1945, I, 294.

<sup>37</sup> S. S. Kocatopcu, *ibid.*, 65; B., 1945, I, 187.

<sup>38</sup> Cf. R. P. Heuer and A. E. Fitzgerald, *Met. and Alloys*, 1944, 19, 1405; 20, 68; B., 1945, I, 101.

<sup>39</sup> *Ibid.*, 1943, 18, 1326; B., 1944, I, 400.



be less than 15 g. per 100 c.c. of water at 50°. <sup>40</sup> The properties of direct-arc electric furnace refractories in relation to furnace operating conditions and construction are discussed by E. K. Pryor <sup>41</sup> and some useful data on causes of roof failure are given. In the case of glass-tank regenerator refractories a wide range of refractories has been tried, including silica, super-duty fireclay, high-alumina, magnesite, forsterite, and chrome refractories. <sup>42</sup> The 40—45% alumina brick is probably the most widely used, but the high-alumina (50—60%) are also popular for chequer service, but it is not always the case that their higher alumina content compensates for their greater porosity. Corundum is, of course, a usual constituent of such bricks. Magnesite refractories have not yet proved very successful. Spalling and relative lack of strength under load at high temperatures are their weakest points. Forsterite bricks, on the other hand, with their high strength under load at high temperatures, high refractoriness, and suitable chemical composition, seem likely to be increasingly used in glass-tank construction where conditions are severe. Not only have they established themselves already for chequer construction, but their use has also now been successfully extended to complete port walls and crowns. It is obvious, of course, that physical and chemical properties of slags are of primary importance in relation to the life of refractories in service, and up to the present work has been concentrated on the viscosity rather than on other properties of slags. The CaO-FeO-SiO<sub>2</sub> ternary system is of great importance in metallurgy since many slags contain these oxides in considerable amounts, and in addition the system may be met when studying the behaviour of refractories in steel furnaces. Recently a number of compositions in this system have been described. <sup>43</sup> These include the minerals fayalite 2FeO, SiO<sub>2</sub>, iron monticellite CaO, FeO, SiO<sub>2</sub>, and three compositions in the metasilicate series of solid solutions between wollastonite CaO, SiO<sub>2</sub> and FeO, SiO<sub>2</sub>. Some interesting work has been carried out on the use of raw topaz as a high-temperature bond for raw and calcined kyanite. <sup>44</sup> Combinations of topaz (not less than 10%), kyanite, and synthetic mullite-corundum are being used as a substitute for Indian kyanite to some extent. <sup>45</sup> A super-duty lightweight refractory of the approximate composition calcined kyanite 70, raw topaz 20, and plastic kaolin 10%, together with 20—30% of powdered anthracite, shows a pyrometric cone equivalent of not less than 37, and only 2% volume shrinkage on a re-heat test at 1600°. A standard 9-in. brick weighs only 5 lb. <sup>46</sup>

<sup>40</sup> Titanium Alloy Manufg. Co., B.P. 569,078; B., 1945, I, 258. U.S.P. 2,323,951; B., 1945, I, 225.

<sup>41</sup> *Trans. Amer. Found. Assoc.*, 1944, 51, 878; B., 1944, I, 400.

<sup>42</sup> C. A. Brashares, *Bull. Amer. Ceram. Soc.*, 1944, 23, 286; B., 1944, I, 400.

<sup>43</sup> G. R. Rigby, B. G. H. Lovell, and A. T. Green, *Trans. Ceram. Soc.*, 1945, 44, 37; B., 1945, I, 258.

<sup>44</sup> T. N. McVay, W. W. Galbreath, and D. Allen, *J. Amer. Ceram. Soc.*, 1944, 27, 275; B., 1945, I, 26.

<sup>45</sup> Cf. C. W. Fyfe, *Indust. Heating*, 1944, 11, 610; B., 1944, I, 400.

<sup>46</sup> W. W. Galbreath, jun., T. N. McVay, and D. Allen, *J. Amer. Ceram. Soc.*, 1944, 27, 241; B., 1944, I, 400.



The cause of the bonding effect of topaz is not yet clear. It has been attributed to volatile constituents in the raw topaz which leave at 1000—1200° and are absorbed by the kyanite, but this is not yet well established. Work has been continued on the action of alkalis on refractory materials.<sup>47</sup> Cone deformation studies of the systems  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  over a limited range, and with and without addition of 2% and 5% of  $\text{Fe}_2\text{O}_3$ , confirmed conclusions arrived at previously<sup>48</sup> as to the greater softening effect of  $\text{Na}_2\text{O}$  (except at very high silica contents) on silica and fireclay materials. They also confirm a finding of some interest, that a material containing 85%  $\text{SiO}_2$  is attacked more readily by alkali than mixtures containing a lesser or a greater proportion of silica.<sup>49</sup> A discussion on the composition, structure, and properties of alumina-silicate refractories is given by J. H. Chesters.<sup>50</sup> A range of alumina content of 20—70%  $\text{Al}_2\text{O}_3$  is considered, of refractory clays and firebricks, and the summary of physical structures and properties in relation to the applications is very useful. A discussion of the production and application to steelworks refractories of high-alumina bricks is also given. A modified procedure<sup>51</sup> for making high-alumina refractories having a bulk density more than 2.24 suggests the use of hydrated alumina which is calcined and mixed with 7—30% of uncalcined clay (containing 60—75% of silica) and fired above cone 10. The firing is stopped when the refractory is still capable of further expansion on reheating. After reheating at 1600° for 5 hours the product will occupy a volume between 99 and 102% of its original volume, and have a bulk density more than 2.24. Some evidence on the value of the panel spalling test in relation to behaviour under service conditions<sup>52</sup> has confirmed the direct practical relationship this test has to service conditions. In the U.S. Navy report it is quoted that the application of this test has reduced spalling from a major to a minor cause of boiler failure. The water-quenching test is often not related to the actual behaviour in service (though this is not true of air quenching), but the panel test appears to correlate satisfactorily such factors as refractoriness, elasticity, and thermal shock-resistance. An analysis of the value of the re-heat (after expansion) test at 1400° on bricks of varying degrees of pre-firing and made by different processes is discussed by E. C. Petrie and C. P. Walters.<sup>53</sup> They confirm the point that the re-heat test will not

<sup>47</sup> F. H. Clews, H. M. Richardson, and A. T. Green, *Trans. Ceram. Soc.*, 1945, **44**, 21; B., 1945, I, 224.

<sup>48</sup> Cf. B., 1942, I, 266.

<sup>49</sup> Cf. also R. E. Birch and M. P. Hall, *J. Amer. Ceram. Soc.*, 1944, **27**, 239; B., 1944, I, 400.

<sup>50</sup> *Iron Age*, 1944, **153**, No. 23, 48; No. 24, 79; B., 1945, I, 155.

<sup>51</sup> A. E. Fitzgerald, Assr. to General Refractories Co., U.S.P. 2,325,181; B., 1945, I, 258.

<sup>52</sup> W. T. Tredennick and J. F. Kelly, *Bull. Amer. Ceram. Soc.*, 1944, **23**, 460; B., 1945, I, 129. L. C. Hewitt, *ibid.*, 372; B., 1945, I, 65. R. A. Heindl and W. L. Prendergast, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 73; B., 1945, I, 224.

<sup>53</sup> *Bull. Amer. Ceram. Soc.*, 1944, **23**, 464; B., 1945, I, 128.



eliminate under-fired first quality firebricks if they show secondary expansion, nor also under-fired super-duty bricks showing no secondary expansion. An interesting and important lead on the development of highly permeable refractories has recently been published.<sup>54</sup> Tests on a furnace lined with a refractory of high permeability have shown the possibility of great savings in fuel, by withdrawing the gases by means of a fan connected to the space between the lining and the backing wall, through the permeable refractory. In this way the gases pass on part of their heat to the refractory instead of the flue. Estimated savings of 40% are suggested by the experimental work, but the available high-temperature refractories of sufficient permeability are not very satisfactory at temperatures above 1400°.

#### ANALYTICAL AND PHYSICAL MEASUREMENTS.

Increasing attention is being paid to the practical development of thermal analysis of clays, especially refractory clays. The method has already proved its worth. S. Speil<sup>55</sup> discusses the application of the method to the beneficiation of bauxite by the Bayer process since diaspor and kaolinite can be readily distinguished from gibbsite. There is less certainty in the determination of montmorillonite owing to variation in the peak with the source of the sample. The grain size of the material under examination affects the peak temperature and the peak area, and a recommendation is made that the particle size fractions of any given sample should be investigated separately, a procedure which would considerably prolong the test procedure.<sup>56</sup> The relationship of moisture expansion to freedom from crazing in service is illustrated by recent work,<sup>57</sup> showing that autoclaving causes a moisture expansion similar to that obtained by three years' storage under ordinary conditions. An interesting point also established is that the moisture expansion of glazed specimens having a craze-resistant glaze was greater than that of the unglazed specimens, while specimens glazed with a crazeable glaze (high expansion) had the same moisture expansion as the unglazed specimens.

An important point, often overlooked, is that of the statistical control of accuracy in routine analysis. It is useful to have a knowledge of the standard error of any analytical method and good evidence that the systematic error is relatively small. H. G. MacColl<sup>58</sup> suggests that the internal control of error can be achieved by analysing samples from one or more control sub-standards with every routine batch. If there is also a question of control between two laboratories, then there should be a regular exchange of routine samples between the two laboratories.

<sup>54</sup> R. H. Anderson, D. C. Gunn, and A. L. Roberts, *J. Inst. Fuel*, 1944, 17, 169; B., 1945, I, 366.

<sup>55</sup> U.S. Bur. Mines, 1944, *Rept. Invest.* 3764; B., 1945, I, 128.

<sup>56</sup> Cf. also A. K. Freberg, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 90; B., 1945, I, 27. L. H. Berkelhamer, U.S. Bur. Mines, 1944, *Rept. Invest.* 3762; C., 1945, 73.

<sup>57</sup> H. Thiemecke, *J. Amer. Ceram. Soc.*, 1944, 27, 355; B., 1945, I, 128.

<sup>58</sup> *Chem. and Ind.*, 1944, 418.



In some cases where the agreement of analyses between the buyer and seller involves costs of some magnitude, it has been a matter of agreement in the past to take an average of the result from each of the representative laboratories. In such cases, however, there is naturally a tendency for the one to use methods giving high results and for the other to use a method giving low results, and the average is not necessarily accurate.

Two new developments in the estimation of silica are of interest.<sup>59</sup> Ammonia solution does not decompose the silica-molybdate complex, and on this basis a method is developed for the determination of silica in the presence of phosphates and arsenates by a modification of the benzidine molybdate method. A photometric method, based on the molybdenum-blue reaction for the determination of silica in sodium aluminate solutions and calcined alumina, is also described.

Further attention has been given to rapid methods for the determination of the moisture content of solid materials.<sup>60</sup> The best of the newer methods are electrical in type and use either the conductance or capacitance of the material.

#### FIRING.

The continued pressure on fuel economy is illustrated by various attempts to improve the efficiency of intermittent ovens fired with raw coal. Automatic stokers have shown some advantage in economy, but do not come up to expectations in giving a more even distribution of temperature over the setting.<sup>61</sup> In another case<sup>62</sup> the firemouth of an updraught oven was operated as a producer and the end of the mouth carried to a position farther into the oven so that the bag wall was at a point normally occupied by the first ring, and flue alterations were made to permit preheating of secondary air and the removal of combustion gases to side-wall flues. In addition the kiln was given one course of hot-face insulating brick. The changes caused a fuel economy of about 40%. The application of step grates to the normal type of pottery intermittent oven is also described.<sup>63</sup> The economy resulting from this is not easy to assess, but probably does not amount to 10% in fuel as a maximum.

The interest in tunnel kilns of small cross-section has increased in the war years, due mainly to the greater ease with which intermittent ovens can be replaced by small continuous kilns without disturbance of output and the greater elasticity of several small units as compared with a large single tunnel. The small tunnel may also be incorporated into a straight-

<sup>59</sup> P. M. Marshev, *J. Appl. Chem. Russ.*, 1943, 16, 155; C., 1944, 109. J. A. Brabson, I. W. Harvey, G. E. Maxwell, and O. A. Schaeffer, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 705; C., 1945, 90.

<sup>60</sup> L. Hartshorn and W. Wilson, *J. Inst. Elect. Eng.*, 1945, 92, Part II, 403; C., 1946, 56. A. Allen and W. H. Howe, U.S.P. 2,359,278. W. J. Delmhorst, U.S.P. 2,359,831. L. D. Baver and B. T. Shaw, U.S.P. 2,362,344.

<sup>61</sup> A. Dimsdale and M. Francis, *Trans. Ceram. Soc.*, 1945, 44, 1; B., 1945, I, 224.

<sup>62</sup> Cf. also H. R. Holding, B.P. 562,930; B., 1944, I, 367.

<sup>63</sup> W. G. Barratt and J. Y. M. Halsall, B.P. 566,838; B., 1945, I, 156.



line production unit because of its shorter length.<sup>64</sup> Improvements in the "walking beam" type of kiln are covered by a recent American patent.<sup>65</sup> In electrically heated kilns it is now proposed to mount the heaters on the trucks, preferably in the middle of the ware setting. The heater trucks carry their own switch-gear and two sets of live rails are provided, one for the main heating current and one to operate the switch-gear.<sup>66</sup> The proposal seems to offer a better possibility of even distribution of heat over the setting and also a better synchronising of firing curves for the top and bottom of the setting.

An attempt to avoid the use of carborundum-fireclay resistors in electric firing is made by the use of resistance elements of graphite entirely surrounded by a double shell of refractory material with powdered refractory material in the space between, so that if cracks develop in the shells they will be powder-sealed and the graphite so protected from oxidation.<sup>67</sup> One or two kilns with this device are now in commercial operation and are functioning well. An improvement in glost tunnels used for open firing suggests the prevention of accumulation of glaze (lead sulphate) on roof and side walls by the provision of openings in the roof at suitable points leading to a special heat-insulated flue, which leads to a collecting chamber; auxiliary electrical heating may be provided in the (inaccessible) flue to prevent condensation.<sup>68</sup>

#### CEMENTS.

A number of interesting modifications and adaptations of gypsum (plaster of Paris) cements have been described. It is well-known that a higher plaster to water ratio can be used if a suitable set retarder is present in plaster of Paris. Considerable advantage is obtained by autoclaving the gypsum in the presence of the soluble protein (used as a retarder).<sup>69</sup> The autoclaving is carried out at 120—140° in the presence of soluble proteins such as casein, peptone, or partly hydrolysed keratin. A modification in the usual type of straw- or fibre-reinforced board is suggested.<sup>70</sup> The gypsum plaster is dry mixed with not more than 10% of comminuted cellulose fibres, water is added, and the whole quickly mixed, moulded, and made to set before the fibres begin to adsorb the water. The procedure is designed to improve the strength of the board and additional lightness can be obtained by adding a foam-producing agent.

<sup>64</sup> J. H. Isenhour, *Bull. Amer. Ceram. Soc.*, 1944, 23, 327; B., 1945, I, 24. *Ibid.*, 321; B., 1945, I, 26.

<sup>65</sup> F. W. Brooke and P. d'H. Dressler, U.S.P. 2,320,172; B., 1945, I, 129.

<sup>66</sup> Brit. Brown-Boveri, Ltd., and H. Oswald, B.P. 563,979 and 563,980; B., 1944, I, 401.

<sup>67</sup> B. J. and B. C. Moore, B.P. 563,225; B., 1944, I, 367.

<sup>68</sup> Gibbons Bros., Ltd., and G. Turner, B.P. 568,404; B., 1945, I, 258.

<sup>69</sup> C. L. Haddon, B. J. Cafferata, and Brit. Plaster Board, Ltd., B.P. 562,561; B., 1944, I, 337.

<sup>70</sup> G. D. King, Assr. to United States Gypsum Co., U.S.P. 2,322,194; B., 1945, I, 156.



It is known that an improvement in the strength of gypsum type cements can be obtained by causing acicular interlocking crystallisation, but the material prepared in the normal way does not crystallise easily in this way. A system of controlled dehydration of gypsum designed to give a material particularly suitable for rapid construction in buildings has recently been described.<sup>71</sup> Crushed gypsum is heated with steam or air between 60° and 90° for 30 minutes and later with steam at 124.5° for 8 hours. Dry steam at 140° is then passed over the product, followed by hot air at 160—180° for 4—5 hours. The final heating can be effected by hot flue gases at 220—240° for 3—4 hours. The product before this final heating has a felted structure and sets in 2—3 minutes, the setting being complete in 5—8 minutes. The use of limestone aggregate in cement has been the subject of a good deal of controversy, although many cases of the successful use of the aggregate in large-scale construction are known. Some recent tests on the use of dolomitic limestone of relatively low thermal expansion compared with a silica pebble type aggregate of much higher expansion<sup>72</sup> showed that under repeated temperature cycle (—10° atmospheric temperature) tests the dolomitic type lost 40—50% of their weight, while the silica pebble type lost only 2—3%. Furthermore, the permanent expansion of the dolomite type was 3—4 times that of the silica pebble type. With the usual complete freezing and thawing test the low-expansion aggregate showed even worse comparative results. The work is of interest in showing a possible explanation of the failure of cast concrete containing dolomitic limestone aggregate. Incidentally, it is claimed that a cement can be obtained by heating a Russian dolomite to 800°, grinding it finely, and mixing it with sand.<sup>73</sup> The general conditions governing the destruction of concrete by frost have been reviewed by A. R. Collins,<sup>74</sup> who considers that frost damage is due to the segregation of ice into layers, rather than to the simple expansion of ice in the pores (which latter is the generally accepted view). He compares the lamination of the concrete with the "frost heaving" of soil. Since frost damage is directly related to the porosity of the concrete, it is difficult to see why laminated freezing should occur unless it is merely a combination of water penetration to a restricted depth combined with freezing conditions which do not penetrate the whole structure.<sup>75</sup>

The reaction between alkali in cement and materials used as aggregates has been the subject of a good deal of work in recent years. Generally speaking the reactive aggregates are silica (opaline, chalcedony, chert)

<sup>71</sup> P. P. Budnikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 288; B., 1945, I, 67.

<sup>72</sup> J. C. Pearson, *Amer. Concrete Inst. J.*, 1943, **15**, 33; B., 1945, I, 259.

<sup>73</sup> V. M. Permjakov and V. F. Shuravlev, *J. Appl. Chem. Russ.*, 1943, **16**, 253; B., 1945, I, 67.

<sup>74</sup> *J. Inst. Civil Eng.*, 1944—45, 29; B., 1945, I, 67.

<sup>75</sup> Cf. also N. G. Farmer and G. L. Lindsay, *Eng. News-Rec.*, 1944, **133**, 214; B., 1945, I, 67. E. O. Axon, T. F. Willis, and R. V. Reagle, *Proc. Amer. Soc. Test. Mat.*, 1943, **42**, 981; B., 1944, I, 403.



and siliceous limestones, but there is no very precise definition of what is meant by a high-alkali cement. Usually no trouble is experienced even with reactive aggregates if the cement contains less than 0.6% of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ . The high expansion tendency which results from the alkali-aggregate reaction with subsequent deterioration has a considerable time lag and simulative laboratory tests are therefore difficult.<sup>76</sup> On the other hand, E. C. E. Lord<sup>77</sup> finds that the effect of tar, ammonium fluosilicate, and sodium hydroxide on the alkali-resistance of concrete when examined under laboratory test conditions gave similar results to those extending over two years under service conditions. The effect of active silica on the lime-solubility of Portland cement in water saturated with carbon dioxide shows that a certain amount of inhibition of lime-solubility occurs, but it is insufficient to have much practical importance.<sup>78</sup> A new zinc phosphate cement of very high volume constancy has been described<sup>79</sup> together with details of its preparation; the hardness and volume constancy of the cement are very good and it should be of commercial interest.

<sup>76</sup> C. O. Hutton, *New Zealand J. Sci. Tech.*, 1945, **26**, B, 191; B., 1945, I, 259.  
R. F. Blanks and H. S. Meissner, *Proc. Amer. Soc. Civil Eng.*, 1945, **71**, 3; B., 1945, I, 156.

<sup>77</sup> *Publ. Roads*, 1944, **23**, 282; B., 1945, I, 102.

<sup>78</sup> R. Zollinger, *Zement*, 1943, **32**, 187; B., 1945, I, 102.

<sup>79</sup> A. Dobrowsky, *Chem. Technik*, 1942, **15**, 159; B., 1945, I, 157.



# IRON AND STEEL.

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FOLLOWING the end of hostilities with Germany and Japan, it is now possible to give a statement regarding the iron and steel production during the past year. The position has been summarised by the *Iron and Coal Trades Review*,<sup>1</sup> where the following data for the war years are compared with the average of the three previous years, 1936-38 :

PIG-IRON AND STEEL PRODUCTION.

Year.	Pig iron.	Steel.
	<i>tons.</i>	<i>tons.</i>
1936-38 average .. ..	7,658,500	11,722,100
1939.. ..	7,979,000	13,221,300
1940.. ..	8,204,600	12,975,300
1941.. ..	7,392,500	12,312,200
1942.. ..	7,725,600	12,941,700
1943.. ..	7,186,900	13,031,200
1944.. ..	6,736,500	12,142,200
1945* .. ..	7,130,000	11,808,000

\* Estimated on the basis of the official figures for the first eleven months of the year.

Whilst the table shows substantial increases, particularly in steel production, during the war years, it does not give an adequate picture of the change that the war produced. This change was greatest in the output of alloy steel required for war purposes, *e.g.*, for shell steel, armour plate, gun forgings, bomb castings, aeroplane construction, etc., such that whereas the output of alloy steel prior to the war was about half-a-million tons per annum, a peak level of 1,595,600 tons was reached in 1943. The increase was the more remarkable by the fact that the steel industry lost some 100,000 of the younger men to the forces, a large proportion of this number being replaced by female labour. Imports of high-grade ore shrank from 5,240,000 to 1,894,000 tons between 1939 and 1943, but with the advent of Lease-Lend, imports of iron and steel exceeded 4 million tons in 1941.

Before the end of hostilities it was realised that the industry would need overhauling since it had not been possible to make many alterations to plant, which indeed had also been severely overworked. A five-year plan envisaging a capital expenditure of about 150 million pounds was put into being to embrace the provision of new coke ovens, blast furnaces, steel-melting furnaces, and rolling mills, the installation of continuous hot strip rolling mills, and the first universal beam mill to be erected in

<sup>1</sup> *Iron and Coal Tr. Rev.*, 1946, 152, No. 4063, 6.



this country. The projects have in mind increased technical efficiency, reduced costs of production, and an increase in annual ingot capacity from 14 to 17 million tons per annum.

In March, 1945, the British Iron and Steel Federation adopted a new constitution based on the principle of self-government within the framework of government policy, for the purpose of organising the industry, institution of scientific research, and for maintaining contacts at the highest level. A guaranteed income of £400,000 per annum assures that research work will not be hampered for lack of funds.

### PRODUCTION.

Modern blast-furnace design and operation are discussed by J. Dale.<sup>2</sup> He states that the American type of blast furnace which has been installed in many countries can be regarded as the modern type. The important characteristics of the coke used in blast furnaces are: porosity, resistance to abrasion, hardness, and cell structure. Iron ore is crushed to a size depending on its density, which is a close indication of its reducibility. The limestone used should be low in silica, a typical composition being: CaO 54.2, MgO 0.35, SiO<sub>2</sub> 0.64, Al<sub>2</sub>O<sub>3</sub> 0.32, FeO 1.0, S 0.05%. The distribution of raw materials in the furnace is described in detail, and the factors governing rate of blowing are analysed. Blast-furnace, blowers, tuyères, stockline protection, hearth and sequence-charging control are discussed.

Rules and formulæ for calculating blast-furnace dimensions are discussed by O. R. Rice.<sup>3</sup> The size of the hearth is related to the coke consumption by the proposed figure of 6300 lb. of coke charged per day per sq. ft. of the annular area extending 6 ft. in front of the tuyères. The number of tuyères is governed by spacing them at about 4 ft. circumferential distance between centres; this gives from 8 tuyères for a 12-ft. hearth to 22 tuyères for a 30-ft. hearth. The inside diameter of the top of the furnace should be such that the area equals the active area of the hearth, i.e., the annular area extending 6 ft. in front of the tuyères. The greater is the volume of a furnace the longer will it take a given quantity of gas to travel from the tuyères level to the stockline, and, within certain limits, the more efficiently will the gas react with the ore. For normal practice with a burden of Lake Superior ore the time (seconds) the gas is retained in the furnace is  $185 \times$  the furnace volume (cu. ft.) divided by the coke consumed per day (lb.). The coke consumed per 2000 lb. of iron can be calculated from  $1000[2 - (20V \div \text{lb. of coke per day})]$ , where  $V$  is the furnace volume (cu. ft.). G. Bulle<sup>4</sup> gives detailed drawings and constructional notes of standard forms of blast furnace, incorporating all the most recent ideas on the subject and aiming at the minimum weight of steel and refractory. Compared with

<sup>2</sup> *J. West Scotland Iron & Steel Inst.*, 1943-44, 51, 45; B., 1944, I, 404.

<sup>3</sup> *Blast Furn. Steel Plant*, 1944, 32, 114, 221; B., 1945, I, 30.

<sup>4</sup> *Stahl u. Eisen*, 1944, 64, 285; B., 1945, I, 158.



conventional German furnaces, these newer forms require 43% less iron and 27% less refractory, and are claimed to have a lower coke consumption and higher output. T. P. Colclough<sup>5</sup> considers that higher efficiency in the combustion of the carbon within the furnace, and greatest possible reduction of the weight of the slag-forming oxides charged in the burden, would lead to considerable economies in coke consumption. He recommends that British ores be mixed, crushed, and graded, and charging based on ore size rather than on ore quality. All fines should be removed from the mixture and sintered before use in the furnace. A miniature blast furnace, constructed for research purposes for the Iron and Steel Industrial Research Council of the British Iron and Steel Federation, is described by G. H. Goodwin.<sup>6</sup> The furnace hearth is 21 in. in diameter and the height 10 ft. It was charged with Northamptonshire ore, and while in use for 13 weeks produced 60 tons of iron, consuming 36—45 cwt. of coke per ton. A report is presented by H. Marenbach<sup>7</sup> of the results of trials with a small blast furnace (41 ft. high, with a hearth 5 ft. 5 in. diameter) in the production of ferro-chromium. The burden consisted mainly of ores containing up to 27% of chromium, and high in alumina and magnesia. A process was developed by which 30—40% ferro-chromium could be continuously produced, and it was considered to be a useful alternative to the electric furnace process.

A progress report on the production of sponge iron is presented by R. S. Dean.<sup>8</sup> The process involves the reduction of ore without simultaneous alloying of the iron with sulphur, phosphorus, carbon, or silicon, and succeeds only if the temperature of reduction is less than the melting point of iron. Direct (*i.e.*, non-alloyed) iron may be obtained by ore purification before reduction, by purification of the sponge iron after reduction, or by removal of impurities as slag. The Bureau of Mines two-diameter rotary-kiln method of making sponge iron is described, and the utilisation of sponge iron in the manufacture of wrought iron and steel is discussed.

#### FOUNDRIY PRACTICE.

The influence of steel mixes and inoculants in grey cast iron have been studied by W. Barnes and C. W. Hicks.<sup>9</sup> The inoculants used were calcium silicide, ferro-silicon, aluminium, ferro-silicon mixed with aluminium, and nickel shot. The following conclusions were reached: (1) increasing the percentage of steel in the cupola charge (*a*) raises the tensile and transverse strengths, (*b*) gives greater stability to ferro-silicon carbides in grey iron so that its physical properties can be improved by oil-quenching and tempering, and (*c*) improves the internal soundness of heavy sections of castings, thus improving the machined finish;

<sup>5</sup> *J. Iron & Steel Inst.*, 1944, 150, 359F; B., 1945, I, 30.

<sup>6</sup> *Iron & Steel*, 1945, 18, Jan., 16; *Bull. I.S.I.*, March, 1945, 121A.

<sup>7</sup> *Stahl u. Eisen*, 1945, 65, 57; B., 1946, I, 137.

<sup>8</sup> *U.S. Bur. Mines*, 1945, Rept. Invest. 3790; B., 1945, I, 191.

<sup>9</sup> *Found. Tr. J.*, 1944, 73, 287, 313, 337; B., 1945, I, 32.



(2) the melting of steel scrap in the cupola is not difficult and the cost is much less than when refined irons are used; (3) although addition of 1% of nickel appears to refine graphite in iron made with a small percentage of steel, its effect on graphite in the higher steel mixtures is negligible; the increase in tensile strength does not justify the marked increase in cost; (4) with grey iron at the spout, normal silicon-base inoculants appear to act as deoxidising agents and the metal is improved by a small addition; addition of aluminium alone has a greater scavenging action than a silicon addition; (5) correct melting practice makes the melting of steel mixtures simple, and special cupolas are unnecessary.

R. Stolle<sup>10</sup> discusses factors affecting desulphurisation with soda ash. Tests with sodium carbonate in an inverted crucible resting on the bottom of a ladle were made in such a way that when iron was poured in the reaction took place under the pressure set up by the gases generated; the iron tapped from the bottom of the ladle contained only 0.002—0.005% of sulphur, whilst a spoon sample from the top contained 0.11%. Additions of 25, 30, and 35 kg. of sodium carbonate to 3500 kg. of iron in the ladle reduced the sulphur content by 45.8, 51, and 57.2% respectively. The optimum quantity of sodium carbonate is generally about 10 kg. per ton of iron.

The conditions which exist in a fully charged cupola have been investigated by N. E. Rambush and G. B. Taylor.<sup>11</sup> Combustion was stopped by shutting off the blast and pouring water through the charging door. The condition of the burden at nine levels is illustrated. It has been established that the relative position of charged materials is not maintained during descent, the shape and size of the metallic pieces in the charge govern the manner of descent, the coke is progressively reduced in size, but not uniformly across a horizontal plane, and the rate of melting of the metallic constituents is mainly governed by their shape and weight as well as by their melting temperature.

The first report on the basic cupola is presented by the Melting Furnaces Sub-Committee of the Institute of British Foundrymen.<sup>12</sup> The use of stabilised dolomite clinker and other basic materials for lining cupolas was studied. When working a cupola so that desulphurisation is obtained, *i.e.*, with a minimum of oxidation and producing iron containing total carbon 2.8 and silicon 1.5%, the life of the lining in the combustion and melting zones was 12—16 weeks; the lining in the well withstood 26 weeks' operation, during which about 4000 tons of metal were melted. Studies on dephosphorisation of iron in basic-lined cupolas for steel-making by the cupola-converter process indicate that: (a) steel scrap higher in phosphorus can be used, (b) higher-phosphorus pig iron can be used instead of hæmatite in the cupola charge, (c) steel can be produced lower in phosphorus than that normally obtained from the acid-lined

<sup>10</sup> *Giesserei*, 1944, 31, 21; B., 1945, I, 103.

<sup>11</sup> *Inst. Brit. Foundrymen*, June, 1945, Paper 826; B., 1945, I, 261.

<sup>12</sup> *Found. Tr. J.*, 1944, 74, 25, 55, 71; B., 1945, I, 158.



converter, and (d) the process has the advantage of off-setting the increase in phosphorus which occurs in the steel produced because of the metallic losses in the cupola and converter. No abnormal pick-up of carbon was noted when operating basic-lined cupolas under conditions favourable for desulphurisation.

The Foundry Practice Sub-Committee of the Steel Castings Research Committee<sup>13</sup> in their first report state that the most important factors governing the feeding of steel castings and the formation of cavities are the ferro-static pressure in operation, the dimensions of runners, the location of runners, and the shape and size of castings. In comparative experiments in making steel castings these factors must be kept constant. The casting of numbers of 6-in. cubes has been carried out with variations in type of head, use of external chills, use of heads lined with insulating mixtures, and variation in gating. It has been found advantageous to secure differential rate of cooling by the use of an insulating lining in the head and external chilling of the casting body. Experiments suggest that hot steel poured slowly gives less piping than cold steel poured rapidly. The casting of ingots with horizontal feeding has shown that the longer is the casting in relation to its cross-section the less is the percentage of head required. The "whirl-gate" head method of feeding steel castings has been investigated. Feeding compounds which are added to the fluid steel as it rises into the heads are summarised, viz., heat-evolving types containing aluminium powder and iron oxides, finely-ground furnace slag with charcoal, papier-maché shapes, chopped straw, impure blacklead, and finely-ground coke or coal. Defects which occur in steel castings and are influenced by composition, fluidity, and design are: shrinkage, cracks, hot tears, internal shrinkage fissures, and internal laps. Cracks which are controlled by composition, design, and after-treatment are "clinks" caused by release of casting stress, by local heating, or by heavy machining. The hot-tearing of castings can be reduced by using steel of low sulphur content.

The hot strength, retained strength, and expansion of (a) new sand cores bonded with organic binders without any clay, and (b) black sand cores containing clay bonded with organic binders, have been studied by E. Pragoff and C. P. Albus.<sup>14</sup> The method of measuring the hot strength of moulding sands is applicable to (b) but not to (a). In new sand cores almost all the strength provided by organic binders is lost after 10 minutes at 538°. Retained-strength tests are valuable when selecting materials to make cores which are easily knocked out. The hindered-expansion method of determining the expansion of moulding sand is not suitable for testing new sand cores containing organic binders alone; it is practical for control tests on black sand cores containing clay.

The effect of changes in the properties of moulding sand mixtures on

<sup>13</sup> *J. Iron & Steel Inst.*, 1945, 151, 329P; B., 1945, I, 191.

<sup>14</sup> *Trans. Amer. Found. Assoc.*, 1944, 51, 935; B., 1944, I, 406.



the quality of iron castings is discussed by G. W. Nicholls.<sup>15</sup> All sands require a water content of 5—6% for green-sand work and 8—10% for dry-sand work. The amount depends on the grain size of the sand and the quantity of coal dust added. The effects of coal dust additions to sand at high temperature are indicated by the following data : at 1200° 10 vol.-% of coal added to the sand produced 390 c.c. of gas from 10 g. of mixture ; with no coal addition the same sand mixture generated 65 c.c. of gas. The coal addition slightly increased the green strength at room temperature and decreased the permeability. Typical casting defects due to generation of too much gas by too much core oil, and to bad venting, are described.

An attempt has been made by R. W. Grimshaw and A. L. Roberts<sup>16</sup> to identify the principal mineral constituents of the kaolinite and montmorillonite types of bonding clays. Observation of the characteristic thermal changes which take place when some clay minerals are heated was the principal method used, and was supplemented by chemical analysis, micro-examination, re-hydration studies, and measures of density.

V. Paschkis<sup>17</sup> explains the theory of the heat-flow analyser and its application to the study of the freezing of iron in sand moulds. The case selected is that of a cylinder 10 in. in diameter and 15 in. high, with a feeder head (above it) 8 in. in diameter and 6 in. high ; between the two there was a core or gate with an opening 2 in. in diameter in one test and 3 in. in another. Cooling curves for various points in the casting and in the mould are given. The size of hole in the core had little effect on the cooling rate of the casting.

The use of cement dust in green-sand moulds to eliminate the drying of moulds is described by K. Alber.<sup>18</sup> Before inserting the cores, the mould is dusted over to a thickness of about 0.5 mm., depending on the amount of water in the sand ; the drag requires a little more cement dust than the cope. It is claimed that when the mould is so prepared the iron is "quieter" on pouring and the castings have a smoother surface when knocked out.

Application of radiography to improvement of foundry technique is described by R. Jackson.<sup>19</sup> The principles involved in the taking and interpretation of a radiograph of a casting are given. The defects which may be detected in castings are : thread-like shrinkage cavities, blow-holes, non-metallic and metallic inclusions, surface defects, and cracks. Accurate quantitative evaluation of such defects is not yet possible. Methods of applying radiography to improve the quality of castings are described.

<sup>15</sup> *Found. Tr. J.*, 1944, **73**, 85, 111 ; B., 1944, I, 406.

<sup>16</sup> *Inst. Brit. Foundrymen*, June, 1945, Paper 822 ; B., 1945, I, 261.

<sup>17</sup> *Trans. Amer. Found. Assoc.*, 1945, **52**, 649 ; B., 1945, I, 261.

<sup>18</sup> *Gießereipraxis*, 1944, **65**, 106 ; B., 1945, I, 261.

<sup>19</sup> *J. Iron & Steel Inst.*, 1945, **151**, 225P ; B., 1945, I, 131.



The influence of centrifugal casting on structure and properties of steel has been studied by L. Northcott and D. McLean,<sup>20</sup> on thick cylinders of a nickel-chromium-molybdenum steel, using chill moulds (without cores) and horizontal rotation. The rotational speed of the mould is the most important factor. Low speed (450 r.p.m.) leads to sharply defined zoning in the casting, whilst medium speed (650 r.p.m.) gives castings relatively free from segregation. Vibration becomes considerable at speeds more than 1450 r.p.m. and causes a circumferential-line type of segregation banding. The influence of casting temperature and pouring speed on segregation is discussed.

### STEEL MAKING.

Tapping equipment in relation to segregation has formed the subject of several investigations. L. O. Uhrus and K. Oberg<sup>21</sup> have studied the erosion of different ladle-nozzle materials by different steels. The nozzle of hand-pressed, de-aired material showed the least wear with all three qualities of steel tapped. Steel containing carbon 0.15 and manganese 1.2% caused much more wear than steels containing carbon 1 and manganese either 1.1 or 0.35%. Some of the steel was tapped into water to form granules and these were sectioned and examined for inclusions; steel containing carbon 1 and manganese 0.35% had the least inclusions. The distribution of inclusions in ingots was also examined. The Bagnall-Bethell ladle nozzle, with which, it is claimed,<sup>22</sup> the rate of teeming can be increased, consists of a single- or multi-nozzle box fixed with a quick-acting bayonet joint below the ordinary nozzle. The orifice in the former is smaller than that in the latter, and when a suitable number of ingots have been poured through the smaller orifice the secondary nozzle box is removed with a rapid movement of a special spanner.

Factors underlying segregation in steel ingots are considered in detail by B. M. Larsen,<sup>23</sup> who concludes that the dendrites branch into the liquid in such a manner as to avoid the need for extra iron atoms to diffuse to the crystallising surface. The columnar habit is encouraged by the presence of solutes with a low diffusion rate which form a low-melting liquid layer around the crystal projections. Large-scale segregation must involve relative motion of the less pure liquid and the dendritic crystals and may be caused by the stirring effect of carbon monoxide formed in the metal or by the settling tendency of unattached dendrites in the less dense liquid in the centre of the ingot. R. M. Brick<sup>24</sup> finds that coring in solid solutions or in combinations of solid solutions and eutectics is the basic cause of segregation. The solidification of nickel-copper, aluminium-copper, and iron-tungsten-chromium-carbon alloys is considered as illustrating typical cored structures. The effects of gas

<sup>20</sup> *J. Iron & Steel Inst.*, 1945, 151, 303P; B., 1945, I, 104.

<sup>21</sup> *Jernkont. Ann.*, 1944, 128, 597; B., 1945, I, 263.

<sup>22</sup> *Iron & Coal Tr. Rev.*, 1944, 149, 841; *Bull. I.S.I.*, Feb., 1945, 100A.

<sup>23</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1764, 13; B., 1945, I, 192.

<sup>24</sup> *Ibid.*, 3; B., 1945, I, 196.



pressure and the forces of contraction and crystallisation in causing inverse segregation are outlined, but they do not explain its occurrence in slush castings; segregation in the liquid phase, resulting from diffusion between the solid and the immediately adjacent liquid layers may be a further factor. Segregation in a 34,000-lb. ingot (C 0.374, Mn 0.66, P 0.10, S 0.015, Si 0.31, Ni 1.86, Cr 0.82, V 0.07, Mo 0.35 average percentage) was studied by S. W. Poole and J. A. Rosa<sup>25</sup> using sulphur-printing and chemical analysis. The ingot was 34 in. square (max.) and was sectioned with an oxy-acetylene torch. All elements segregated. Major segregation occurred in the same general areas throughout the ingot and was apparently of the inverse order. Greatest segregation was shown by carbon, followed by nickel and manganese. In the body of the ingot sulphur and phosphorus did not show the degree of segregation expected. H. L. Walker, E. J. Eckel, J. Hino, and F. H. Mueller<sup>26</sup> attribute the low hardness readings observed at the centre of 2 ft. 4 in. bars of S.A.E.4150 steel to segregation. The effect may be detected by a Jominy test-bar machined from the stock off-centre and provided with flats ground at locations corresponding to the centre and outside of the original material. It is considered that segregation in this steel may be due to the slow rate of dissolution of chromium carbides in austenite; greater uniformity was found in a steel containing C 0.66, Mn 0.59, P 0.017, S 0.024, Si 0.21, and Mn 0.33%. The segregation in a lead-bearing steel ingot, and in a lead-free steel ingot, has been compared by C. S. Graham.<sup>27</sup> The lead-bearing ingot (axial section) showed less segregation of sulphur and a thinner columnar zone. The lead itself was evenly distributed, except at the extreme bottom of the ingot. The relation of open-hearth practice to segregation in rimmed steel has been examined by J. W. Halley and G. L. Plimpton, jun.,<sup>28</sup> who find that the factors which affect segregation include the extent of the solidification range, the removal of constituents such as carbon, manganese, and aluminium as gaseous reaction products or slags and the rate at which they are removed by gas evolution or by the washing action of liquid metal, and the ratio of rim to core. The vigorous metal motion desired to produce a clear rim may be secured by maintaining high values of carbon and oxygen, a rapid freezing rate, and a low pouring temperature. Segregation in the core is minimised by holding the concentration of impurities to a low value, and checking the rimming action as early as possible by capping the ingot.

#### HEAT-TREATMENT AND STRUCTURES.

Procedures for hardening and tempering steel by quenching from the temperature at which the bar leaves the rolling mill are suggested.

<sup>25</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1764, 58; B., 1945, I, 192.

<sup>26</sup> *Met. and Alloys*, 1944, **19**, 346; B., 1945, I, 230.

<sup>27</sup> *J. Iron & Steel Inst.*, 1945, **151**, 273P; B., 1945, I., 192.

<sup>28</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1764, 37; B., 1945, I, 191.



R. Schäfer and W. Drechsler<sup>29</sup> claim that the reheating of billets can be so controlled that the temperature of the bar in the last pass is 920—820°. By quenching the bar in water from this temperature and then tempering, an excellent combination of properties can be obtained. O. Kukla, W. Kuntscher, and H. Sajosch<sup>30</sup> state that by hardening direct from the heat of rolling and then tempering, an improvement of 2—3 m.-kg. per cm.<sup>2</sup> in the notched-bar impact values was obtained on a number of steels, including unalloyed steels containing 0.16—0.52% of carbon. The danger of cracking due to quenching the unevenly heated bars was met by using temperature-indicating colours and withdrawing the bars from the quenching bath at 150—350°; intermediate annealing was unnecessary. The hardening of low-carbon steels in water with no tempering was successfully developed; in this way bars of 50 mm. diameter attained a notched-bar impact strength of 8 m.-kg. per cm.<sup>2</sup> with a tensile strength of 124 kg. per mm.<sup>2</sup> and an elastic limit of 100 kg. per mm.<sup>2</sup> Another successful method of heat-treatment comprised high-temperature diffusion-annealing immediately after the final rolling or forging process; this prevented segregation and internal stresses without the detrimental effects of over-heating. H. Krainer<sup>31</sup> presents a report on tempering by induction heating in the rolling mill. The results were favourable from an economic point of view, as the current consumption was only 140—200 kw.-hrs. per ton of bars. The tests were made on low-alloy chromium-vanadium steel. The impact strength of bars with a tensile strength exceeding 100 kg. per sq. mm. was better than that of bars tempered by the usual processes. The tensile and impact properties of bars tempered by induction heating and by other processes are compared in tables and by series of curves.

Experiments were carried out by A. Pomp and A. Eichinger<sup>32</sup> to determine how storing at room temperature and long-time annealing at 200° affected the appearance of Lüder lines when specimens of seven 0.02—0.2% carbon steels were subjected to tensile tests after quenching in water from 700°. Normally-annealed steel after treatment at 200° for 2000 hours had a clearly defined elastic limit accompanied by Lüder lines. Quenching in water from 700° caused complete disappearance of the plastic range and simultaneously increased the deformation-resistance. Annealing at 200° for only 10 hours caused specimens tested at room temperature to exhibit a definite elastic limit accompanied by very fine Lüder lines. The difference between the elastic limits of the water-quenched, normally-annealed steels, with and without treatment at 200° for 2000 hours, was in some cases quite small, although their lattice constituents differed considerably. Prolonging the annealing time at 200° increased the width of the Lüder bands, but even after 2000 hours' treatment they were narrower than those on normally-annealed specimens.

<sup>29</sup> *Z. Ver. deut. Ing.*, 1944, **88**, 47; B., 1944, I, 407.

<sup>30</sup> *Stahl u. Eisen*, 1943, **62**, 1067; B., 1945, I, 33.

<sup>31</sup> *Ibid.*, 1945, **65**, 95; *Bull. I.S.I.*, May, 1945, 11A.

<sup>32</sup> *Mitt. Kaiser-Wilh.-Inst. Eisenforsch.*, 1943, **26**, 51; B., 1945, I, 35.



J. Sorenson<sup>33</sup> has studied the effect of changing the annealing procedure for a chromium-nickel-molybdenum steel on the life of the high-speed tungsten steel used to turn it. The previous heat-treatment comprised normalising at 870°, heating to 830°, holding at that temperature for 25 hours, and furnace-cooling; that leading to longer tool life consisted of normalising at 900°, heating to 750°, cooling to 655°, holding for 24 hours at that temperature, and air-cooling.

Methods of seasoning or stabilising steels to prevent dimensional changes in service are described by H. A. Knight.<sup>34</sup> After hardening, the parts are cooled to -45° to -100° and reheated to about 150°, the cycle being repeated several times without allowing the work to remain at room temperature. By this treatment, all retained austenite is transformed into martensite and stress concentrations resulting from the transformation are relieved.

E. S. Rowland, J. Welchner, and R. H. Marshall<sup>35</sup> have investigated the effects of varying the heating time from 0 to 240 minutes, and the quenching temperature from 788° to 927°, on the Jominy end-quench hardenability value for a plain 1.03% carbon steel, S.A.E.52100 steel, and "Graph-Mo," a molybdenum-bearing 1.47% carbon steel containing 0.20% of graphite. The changes in hardenability are of the order to be expected from considerations of the rate of dissolution of carbon from the original structure, the grain size, and the number and distribution of nucleating carbides. The number of carbides visible in the microstructure was, without exception, least in specimens treated under conditions which produced the highest hardenability.

The mechanical properties and transformation behaviour of an air-quenched steel (C 0.32, Mn 0.57, Si 0.22, S 0.016, P 0.016, Ni 3.38, Cr 0.65, Mo 0.26%) have been studied at various stages before, during, and after the austenite-martensite change, by A. H. Cottrell.<sup>36</sup> Tensile-testing of specimens in the unstable austenitic condition shows that the steel has a low elastic limit and is ductile, that transformation is induced by plastic strain, and the bainite and martensite produced by the transformation have greater elasticity and less ductility. Martensite obtained by air-quenching has high strength and appreciable ductility.

The effect of previous deformation on decomposition of austenite on chilling has been examined by H. Jolivet and J. de Lacombe.<sup>37</sup> The usual type of curve relating degree of transformation of austenites with temperature shows an inhibition period, then an acceleration, and finally a retardation; whilst this is modified considerably by deformation of the austenite, the application of a load does not alter the kinetics of the process unless a considerable deformation is produced. A previous

<sup>33</sup> *Steel*, 1944, **114**, No. 20, 114; B., 1944, I, 408.

<sup>34</sup> *Met. and Alloys*, 1944, **19**, 610; B., 1944, I, 370.

<sup>35</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1662; B., 1944, I, 408.

<sup>36</sup> *J. Iron & Steel Inst.*, 1945, **151**, 93P; B., 1945, I, 105.

<sup>37</sup> *Compt. rend.*, 1942, **214**, 878; B., 1945, I, 105.



deformation modifies the process even though no load is applied during the course of the transformation. The effect is shown by the decrease, and even complete disappearance, of the inhibition period, and by an acceleration of the initial period, and is due to a large increase in the number of transformation centres. Rate of growth of the centres is not appreciably altered. H. Jolivet<sup>38</sup> has continued his researches on the structural changes resulting from the coalescence of the cementite particles in a steel (C 0.75, Mn 0.7, Cr 1.0, Mo 0.6%) after the following heat-treatments: (a) spheroidisation by reheating at 730° for 3—180 hours after initial isothermal transformations chosen to produce pearlitic (transformed at 720°), troostitic (650°), "granulitic" (550°), and bainitic (400°) structures, respectively; (b) spheroidisation by prolonged heat-treatment at the above various temperatures of isothermal transformation; (c) spheroidisation at 725° for 1½—48 hours after pretreatment (from the normalised state) for 15 minutes at 950°, 900°, 875°, 850°, or 825° so as to take cementite nuclei into solution to a varying extent. The influence of carbide nuclei and the presence of small amounts of vanadium (carbide-forming) and aluminium (which does not form carbides) was also briefly studied.

The transformation of austenite at temperatures within the martensitic zone has been investigated by F. C. Thompson and L. R. Stanton,<sup>39</sup> who find that the tempering curve of a martensitic steel, transformed isothermally, differs radically from that of oil- or water-quenched material. Grain size exerts a considerable effect at the Ar1 point, the steel reacting more rapidly as grain size decreases. Apart from changes in normal composition, the chief factors which affect isothermal treatment results are the degree of deoxidation and existence of sorbitic structure in the material before treatment. J. R. Cruciger and J. R. Vilella<sup>40</sup> give isothermal transformation diagrams for a steel, both uncarburised (0.16% carbon) and carburised to 0.97% carbon, and represent the behaviour of both core and case. Representative photomicrographs of the structures after transformation at 650—370° are reproduced. The uncarburised steel after transformation below about 480° exhibits Davenport's "X" constituent. This appears when proeutectoid ferrite separates out at a comparatively low temperature; the ferrite when formed is presumably supersaturated with carbon, which eventually is precipitated as minute particles.

The production of bainite from 3% chromium steel (carbon 0.38%) has been studied in detail by E. P. Klier and T. Lyman<sup>41</sup> using dilatometric, X-ray, and microscopical methods. Isothermal transformation diagrams are also given for five other low- and medium-alloy steels (containing chromium + molybdenum, uranium, nickel, manganese,

<sup>38</sup> *Rev. Mét.*, 1943, 40, 33, 65; B., 1945, I, 298.

<sup>39</sup> *J. Iron & Steel Inst.*, 1945, 151, 133P; B., 1945, I, 105.

<sup>40</sup> *Trans. Amer. Soc. Met.*, 1944, 32, 195; B., 1944, I, 408.

<sup>41</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1696; B., 1945, I, 70.



and copper, respectively) and three plain carbon steels. The first stage in the bainite reaction is, it is suggested, the formation of alternate regions of high and low carbon content in the austenite. The low-carbon regions transform into supersaturated ferrite by a martensite-like lattice rearrangement, and this product begins at once to decompose, precipitating a carbide of iron in a ferrite matrix to form bainite. The high-carbon regions may remain as retained austenite and may be a cause of the inferior properties reported for some alloy steels transformed in the bainite region.

B. F. Shepherd<sup>42</sup> presents diagrams in which the end-quench hardenability of steel is related to the critical hardenability, *i.e.*, the diameter of bar which will have a 50% martensitic structure at the centre after quenching in still oil, and to the hardness obtained after tempering at various temperatures. The application of these diagrams for determining the cooling rates and tempering temperature for obtaining the desired surface and core hardness is explained.

The existence of a second phase in the iron-chromium system has been confirmed by A. J. Cook and F. W. Jones,<sup>43</sup> and the phase boundaries have been established by X-ray examination. Above 820°, the  $\alpha$  phase is stable; at 820° the 50% chromium alloy transforms to the  $\sigma$  phase; at 600° alloys containing 44–50% of chromium consist of  $\sigma$  and alloys with 26–44 and 50–71% of  $\alpha + \sigma$ . The transformations are sluggish, particularly in the range 770–820°, where a hysteresis effect appears to exist, but can be accelerated by cold-working.

The use of lithium to keep furnace atmospheres neutral, and entirely free from water vapour, is discussed by C. R. Thomas.<sup>44</sup> A description is given of a small muffle furnace in which a partly burned gaseous fuel is first used to vaporise lithium so that the mixture enters the muffle containing the parts to be heat-treated. The reactions of lithium with water vapour, oxygen, and carbon monoxide are explained, and it is shown that there can be no water vapour in the atmosphere with lithium present, and in this dry state the atmosphere is inert so that steels of different carbon content can be treated without oxidation or loss of carbon.

W. Betteridge<sup>45</sup> describes the nitriding of a steel containing Ni 12, Mn 6, Cr 4.5, and V 0.3%, which was not successful by ordinary methods, as the hardened surface was spoiled by flaking of the outer layers of the case. Crystallographic examination showed that this was due to the presence of  $\text{Fe}_4\text{N}$ , which, in addition to flaking away, was softer than the underlying layers of  $\gamma$  solid solution. If at the surface a nitrogen content could be obtained which was just too small to allow the formation of  $\text{Fe}_4\text{N}$ , flaking would be avoided and the hardness would

<sup>42</sup> *Met. Progr.*, 1944, **45**, 503; *B.*, 1944, **I**, 407.

<sup>43</sup> *J. Iron and Steel Inst.*, 1943, **148**, 217P; *B.*, 1945, **I**, 300.

<sup>44</sup> *Ind. Heating*, 1944, **11**, 1405; *Bull. I.S.I.*, Oct., 1945, 78A.

<sup>45</sup> *J. Sci. Instr.*, 1945, **22**, 28; *B.*, 1945, **I**, 160.



still be adequate. This was achieved by holding the steel parts at  $600^{\circ}$  for 6 hours after cutting off the flow of ammonia to the nitriding chamber, thus giving the nitrogen time to diffuse inwards and reduce the concentration at the surface. I. A. Binder<sup>46</sup> gives a description of the nitriding process as applied to the stems of 14/14 chromium-nickel steel exhaust valves for internal-combustion engines. The case obtained is only 0.004—0.006 in. deep after 50 hours' treatment at  $538^{\circ}$  in partly dissociated ammonia, but this hardened surface considerably reduced the wear by contact with the guide. Methods of reducing ammonia consumption in the nitriding of steels are given by C. V. Snell.<sup>47</sup> A 60% drop in consumption occurs if the composition of the inflowing gases is so adjusted as to give 60% of dissociated ammonia in the exhaust gases; dissociation may be allowed to increase to 85% without detriment to the case if a preliminary nitriding at 30% dissociation has been in force for a short time. By using a high ammonia dissociation the "white layer" may be eliminated. At lower temperatures ( $940$ — $950^{\circ}$ ) ammonia consumption is lower by 20%, the Rockwell hardness higher, and the case depth reduced. The gas pressure in the nitriding chamber should be kept at 1 in. of water. Descriptions are given<sup>48</sup> of two nitriding processes, the "Maxi" and the "Holden Hy-Speed Case" treatments. The former consists primarily of nitriding the surface of high-speed steel tools after they have been hardened, tempered, and finish-ground. The salt used is a eutectic mixture of sodium and potassium cyanides which is applied to the tools at  $550$ — $565^{\circ}$ . The latter is a liquid-bath nitriding treatment similar to that applied by commercial liquid-salt baths. The relationship between preliminary heat-treatment and response to nitriding of some nitriding steels has been investigated by C. C. Hodgson and H. O. Waring,<sup>49</sup> who find that the preliminary heat-treatment to which a steel has been submitted may influence considerably the maximum hardness attained during nitriding. Chromium-molybdenum steels (C 0.18—0.27, Ni 0.22—0.30, Cr 1.23—3.10, Mo 0.52—0.69%) and chromium-molybdenum-vanadium steel (C 0.38, Ni 0.08, Cr 1.90, Mo 0.30, V 0.18%) are considerably affected by the pre-nitriding tempering treatment. A chromium-molybdenum-aluminium steel (C 0.27, Ni 0.25, Cr 1.62, Mo 0.31, Al 0.86%) was not affected by any pre-nitriding heat-treatment.

#### PROPERTIES AND TESTING.

The effect of additions of thorium to three low-alloy steels (alloyed with vanadium, chromium, and molybdenum, respectively) and one plain carbon steel, all containing about 0.3% of carbon and about 1.8% of manganese, has been studied by H. Cornelius.<sup>50</sup> The effect of adding

<sup>46</sup> *Machinist*, 1944, 88, Dec. 30, 102; *Bull. I.S.I.*, Feb., 1945, 105A.

<sup>47</sup> *Met. Progr.*, 1944, 48, 299; B., 1945, I, 160.

<sup>48</sup> *Machinery*, 1944, 65, Dec. 7, 627; *Bull. I.S.I.*, Feb., 1945, 105A.

<sup>49</sup> *J. Iron & Steel Inst.*, 1945, 151, 55P.; B., 1945, I, 106.

<sup>50</sup> *Arch. Eisenhüttenw.*, 1943, 17, 23; B., 1945, I, 38.



up to 1.4% of thorium to heat-treatable steels is governed primarily by the formation of the very stable carbide,  $\text{ThC}_2$ , which is practically insoluble in solid iron at temperatures below  $1340^\circ$ . In spite of this the hardening temperature range is only slightly extended. The effect of the insolubility of  $\text{ThC}_2$  is that the steel loses its heat-treatability entirely if the thorium content is about 10 times the carbon content, and is sufficient to convert all carbon into  $\text{ThC}_2$ . The presence of large amounts of  $\text{ThC}_2$  in heat-treated steel reduces its toughness. The scaling-resistance of the steels at  $650^\circ$  and  $800^\circ$  was not improved by addition of thorium. If the thorium addition exceeds a few tenths of 1% the effect is likely to be detrimental.

The results of tests on 0.4% carbon steels and on steels alloyed with chromium, nickel, and molybdenum, with and without additions of 0.08% of titanium and 0.005% of boron, are presented by G. F. Comstock.<sup>51</sup> The boron-treated unalloyed steels equalled the alloy steels without boron in their tensile, impact, and machining properties, and were sometimes superior to them in hardenability. T. G. Harvey<sup>52</sup> finds that, in general, additions of 0.002% of boron to 0.4–0.5% carbon, free-machining steel increase the hardenability by 31% and reduce the machinability by about 5%.

The influence of tin has been investigated by J. W. Halley.<sup>53</sup> He reports that tin up to 0.06% in cold-reduced 0.08% carbon rimming steel strip does not affect rolling. Semi-killed 0.23% carbon structural steel containing 0.2 and 0.3% of tin shows some checking in the blooming mill, but is otherwise satisfactory. In both cases tensile strength and yield point are slightly increased, and elongation and impact strength slightly decreased. With 0.4% carbon forging steel, tin additions up to 0.23% affect only impact-resistance. Tin additions up to 0.11% to a 0.77% carbon rail steel cause an increase in tensile strength and Brinell number, and a continuous decrease in ductility as measured by a bend test. The effect of tin additions to steel is similar to that of one fifth the amount of phosphorus.

W. Eilender, H. Arend, and F. Kleinermanns<sup>54</sup> state that additions of up to 0.5% of nickel to steel containing C 0.3, Si 0.33, Mn 1.2, Cr 0.8, and V 0.25% have no effect on the tensile strength, yield point, ductility, notch-sensitivity, or welding properties in any state of heat-treatment. Additions of about 0.08% of aluminium to the steels just before casting produced no marked grain refinement, but made the metal very sensitive to hair-cracking on welding; the use of aluminium as a deoxidiser for these steels should therefore be avoided.

The influence of hydrogen on mechanical properties of some very low-carbon manganese-iron alloys and on Hadfield manganese steel

<sup>51</sup> *Iron Age*, 1944, 154, No. 2, 48; B., 1945, I, 35.

<sup>52</sup> *Ibid.*, 1945, 155, No. 7, 52; B., 1945, I, 299.

<sup>53</sup> *Amer. Inst. Min. Met. Eng.*, 1942, *Tech. Publ.* 1513; B., 1944, I, 371.

<sup>54</sup> *Stahl u. Eisen*, 1943, 63, 824; B., 1944, I, 371.



has been studied by H. H. Uhlig.<sup>55</sup> Low-carbon (0.02—0.03% C) manganese-iron alloys containing 9—22% of manganese readily dissolve hydrogen at 1000° and retain sufficient of the gas on quenching to become seriously embrittled. Electrolytic iron and 3.3% manganese alloy does not retain sufficient hydrogen to be embrittled, and Hadfield manganese steel (Mn 14, C about 1%), although it retains hydrogen, is not embrittled, probably on account of its different ( $\gamma$ ) structure. The dissolved hydrogen is readily removed by vacuum-treatment at 1000°, when all the alloys except those with 6—7% of manganese become ductile. Brittleness of the quenched 6—7% manganese alloys is attributed to a metastable  $\alpha$  phase which transforms into a more ductile equilibrium phase on tempering at 550°. Exposure to cathodic hydrogen in an electrolyte of sulphuric acid embrittles alloys containing 10—14% of manganese, but hydrogen is not appreciably absorbed by other alloys, possibly because their surfaces catalyse the reaction  $2H \rightarrow H_2$ . Other reasons are discussed.

Specimens of a chromium-molybdenum steel containing residual stresses as a result of machining and heat-treatment were examined by A. Schaal,<sup>56</sup> using an X-ray technique, and the stress was determined at increasing depth from the surface. A residual compressive stress of 55 kg. per mm.<sup>2</sup> was determined in the surface layer to a depth of 0.15 mm. On superimposing a tensile stress, the stress in the surface layer was much less than that in the deeper layers; this resulted in the metal beginning to flow below the surface. When a compressive stress is superimposed the residual and applied stresses are additive, with the result that the highest loading is at the surface, where the metal soon begins to flow.

The damping capacity of bars of variously heat-treated steel has been measured by L. Frommer and A. Murray<sup>57</sup> by means of an electromagnetic method of inducing torsional oscillations in the freely suspended bars; the damping value is a characteristic property for the steel in each condition of heat-treatment. E. Scheil and G. Reinacher<sup>58</sup> have studied the  $\gamma \rightarrow \alpha$  transformation in alloys containing 15—29% of nickel by making simultaneous measurements of the elastic modulus and damping capacity. With pure iron, with alloys containing a small percentage of nickel, and with those containing 15—29% of nickel, the transformation is associated with a reduction in the elastic modulus; with alloys containing 10—15% of nickel there is an increase in the elastic modulus. Raising the nickel content lowers the elastic moduli of both  $\alpha$ - and  $\gamma$ -iron. The transformation is accompanied by an increase in the damping capacity, and this corresponds with a similar increase caused by plastic deformation.

<sup>55</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1701; B., 1945, I, 71.

<sup>56</sup> *Z. Metallk.*, 1944, 36, 70; B., 1945, I, 107.

<sup>57</sup> *J. Iron & Steel Inst.*, 1945, 151, 45P; B., 1945, I, 107.

<sup>58</sup> *Z. Metallk.*, 1944, 36, 63; B., 1945, I, 107.



H. Lüpfer and E. Gaiser<sup>59</sup> compare the tensile and impact properties of 10 steels containing Mo nil, Cr 0—2.35, Mn 0.7—1.8, and C 0.26—0.51% with those of a chromium-molybdenum steel containing Mo 0.24, Cr 0.93, and C 0.39%. The materials were tested in the heat-treated condition both parallel with and at 90° to the direction of rolling, and at temperatures of 20° to —60°. The properties of the chromium-molybdenum steel were slightly exceeded by a steel containing V 0.13, Cr 0.99, Mn 0.70, and C 0.47%. A steel containing Cr 1.14, Mn 1.08, and C 0.37% was nearly as good, and one containing Cr 0.14, Mn 1.45, Si 1.14, and C 0.31% should have some application. The others were of relatively little value.

Tests to determine the effect of shot-peening on the properties of metals are described by H. F. Moore<sup>60</sup> and the results discussed. Shot-peening increases the tensile strength of a metal just below the surface and also sets up longitudinal compressive stress in the thin skin of peened metal. A limited amount of peening increases the fatigue strength, but too much peening can be applied and this reduces the fatigue-resistance. The corrosion-resistance of steel is increased by peening. Shot-peening can be applied to parts of irregular shape which might be distorted by heat-treatment and local application is advantageous in such cases as the fillets of shafting where stress concentrations occur. D. C. Turnbull<sup>61</sup> quotes some examples which illustrate how shot-peening increases the fatigue strength of coil springs and gear teeth and describes a method of determining the intensity of peening. If a thin strip of hard steel is peened only on one side the surface fibres on that side are stretched and the strip becomes curved; this curvature increases with additional peening, and a gauge reading in thousandths of an inch has been devised to measure this curvature and thus provide a rapid method of determining peening intensity. The increased use of shot-peening has drawn attention to the selection of the most suitable shot. The properties and structure of chilled iron shot, malleablised chilled shot, and of hardened and tempered iron shot are described and discussed by O. E. Harder and J. T. Gow.<sup>62</sup>

The effect of variables on creep-resistance of steels has been investigated by H. C. Cross and W. Simmons,<sup>63</sup> continuing previous work by Cross and Lowther (B., 1941, I, 295). Creep tests were made at 454° on a silicon-killed steel, a silicon-aluminium-killed steel, an aluminium-killed non-ageing steel, a rimmed carbon-molybdenum steel, and on plain carbon and carbon-molybdenum weld metal. All the materials were heat-treated to produce fine- and coarse-grained structures for comparison of their creep-resistance. Different heat-treatments and cooling rates producing various grain sizes of austenite and ferrite in a 0.14% carbon

<sup>59</sup> *Metallwirts.*, 1944, 23, 9; B., 1945, I, 299.

<sup>60</sup> *Iron Age*, 1944, 154, Nov. 2, 67, 136; *Bull. I.S.I.*, Feb., 1945, 110A.

<sup>61</sup> *Machinist*, 1944, 88, Dec. 16, 83; *Bull. I.S.I.*, Feb., 1945, 110A.

<sup>62</sup> *Trans. Amer. Soc. Metals*, 1944, 35, 390; *Bull. I.S.I.*, Feb., 1945, 110A.

<sup>63</sup> *Proc. Amer. Soc. Test. Mat.*, 1944, 44, 161; B., 1945, I, 299.



silicon-killed steel had little effect on the creep-resistance; a 0.17% carbon silicon-aluminium-killed steel showed a much better creep-resistance when coarsened and cooled in air. With both steels a heat-treatment which reduced the grain size of the austenite tended to obliterate the effects of a previous coarsening treatment. Cooling in air after coarsening did not produce good creep-resistance in an aluminium-killed non-ageing steel, but faster cooling in water produced a very low creep rate. Addition of molybdenum increased the creep-resistance of rimming steel. Weld metal of plain carbon steel and of carbon-molybdenum steel had creep-resistance equal to or better than that of wrought steel of the same composition which had been heat-treated to produce the optimum creep-resistance. S. Dushman, L. W. Dunbar, and H. Huthsteiner<sup>64</sup> have obtained creep data under conditions of constant creep rate for a number of metals and alloys in the form of wires. The most creep-resistant alloys for high temperature are those containing nickel, molybdenum, chromium, and tungsten. Photomicrographs of longitudinal sections of the elongated wires, which are reproduced, emphasise the intimate relation between grain structure and rate of creep.

Steels tested by E. Siebel and G. Hahn<sup>65</sup> included three chromium steels containing 6, 16, and 23% of chromium, a 23-18 chromium-nickel steel, a steel containing Al 5, Cr 9, and Ti 1%, and one containing Mn 18, Cr 9, and Ni 1%. A special test apparatus was constructed in which hollow specimens with a gauge length of 80 mm., an outside diameter of 8.7 mm., and an inside diameter of 3.5 mm. were heated by their own resistance to a heavy current at temperatures up to 1200° for periods up to 1650 hours. A comparison of the loads required to cause a total creep of 1% at 1000° in the ferritic steels after 1000 hours showed the great superiority of the chromium-aluminium steel; at 900° the manganese-chromium steel gave the highest value. Pretreatment of the 16% chromium steel at 1000° for 500 hours increased the creep strength at 900° by 250%. The fractures in the austenitic steels were intercrystalline whatever the temperature and load; those of the ferritic steels were mostly transcrystalline. There was much more deformation before fracture in the case of the ferritic steels. The direct resistance-heating of the specimens did not appear to affect either the resistance to deformation or the structure.

#### CORROSION AND HEAT-RESISTANCE.

The comparative effect of carbon and nitrogen on intergranular corrosion of 18/8 stainless steel is discussed by H. H. Uhlig.<sup>66</sup> The effect of nitrogen in causing susceptibility to intergranular corrosion is less than that of carbon, but a definite propensity to this effect appears

<sup>64</sup> *J. Appl. Physics*, 1944, 15, 108; B., 1945, I, 131.

<sup>65</sup> *Arch. Eisenhüttenw.*, 1944, 17, 211; B., 1945, I, 264.

<sup>66</sup> *Trans. Electrochem. Soc.*, 1945, 87, Preprint 13, 141; B., 1945, I, 265.



in an 18-8 steel containing nitrogen 0.2 and carbon 0.007% in presence of a hot nitric acid-hydrofluoric acid reagent. This reagent is more severe than the normal test solution containing sulphuric acid and copper sulphate. The maximum magnetic induction of steel containing 0.2% of nitrogen results from annealing at  $700^{\circ}$  as in the case of steel containing carbon. Intergranular corrosion of the nitrogen-containing steel in the nitric acid-hydrofluoric acid reagent is more pronounced after treatment at  $500$ – $600^{\circ}$ . These results could largely be explained by the precipitation of a chromium nitride, but a more comprehensive theory is required to explain the effects of both carbon and nitrogen. An austenitic steel containing Cr 18, Ni 24, C 0.003, and N 0.006% has shown intergranular corrosion in the sulphuric acid-copper sulphate reagent after prolonged treatment at  $500^{\circ}$ . The mechanism of corrosion seems to involve grain-boundary precipitation of a metallic phase.

The corrosion of steels in marine atmospheres and in sea-water has been investigated by C. P. Larrabee.<sup>67</sup> The results of exposure tests at several stations are described, and discussed in conjunction with data from other published work. In marine atmospheres the low-alloy steels are superior to the plain steels, as in industrial atmospheres. The degree of superiority can be found only by tests which closely resemble service conditions. Only the very highly alloyed stainless steels remain untarnished, but the lower grades are only slightly rusted. Zinc-coated steel is quite satisfactory under many conditions. In sea-water the rate of penetration of mild steel varies between 0.002 and 0.0077 in. per year, whilst the average rate for plain and low-alloy steels is 0.004 in. per year. Austenitic stainless steels are liable to pitting unless they are highly alloyed or contain an addition of 2–3% of molybdenum. J. F. J. Thomas and A. C. Halferdahl<sup>68</sup> describe comparative corrosion-resistance to sea-water of low-alloy, high-strength steels. Commercial "mild alloy" steels (C 0.09–0.25, Mn 0.32–1.65, Si 0.03–0.68, Cu 0.22–1.10, Ni nil–1.89, Cr nil–1.00, Mo nil–0.10, P 0.008–0.141, S 0.019–0.034%) have been subjected to corrosion-testing by half-tide exposure of samples at the Atlantic and Pacific coasts, by laboratory salt spray using 3.5% aqueous sodium chloride at  $35^{\circ}$ , total immersion in aerated Atlantic sea-water at  $35^{\circ}$ , and stirring in sea-water. The duration of testing was one year and two years. The tests indicate that small contents of copper, nickel, chromium, and/or molybdenum in mild steel exposed to spray, or to air and sea-water alternately, are beneficial. When subjected to total immersion in sea-water, corrosion of steels containing these elements is greater.

The corrosion rate and relative corrosion-resistance in an unstressed condition of 46 materials, *e.g.*, nickel, nickel-copper, and chromium-nickel steels, and cast iron, used for constructing steam generators, piping, and turbines, have formed the subject of a five-year study reported

<sup>67</sup> *Trans. Electrochem. Soc.*, 1945, **87**, Preprint 12, 123; B., 1945, I, 232.

<sup>68</sup> *Canad. Chem.*, 1945, **29**, 43; B., 1945, I, 192.



by I. A. Rohrig, R. M. van Duzer, and C. H. Fellows.<sup>69</sup> Tests were made under plant-operating conditions, and samples exposed in steam at 380 lb. per sq. in. at 496° and 593° for 4000—16,000 hours. Weight loss, hardness, and metallographic data were obtained after successive exposure periods for many of the samples, and trends in the corrosion rate were plotted. The results show that the loss in weight of plain carbon steel exposed to steam at 593° continues at a high rate, whilst the rate of loss of alloyed materials decreases with time. The high-chromium-nickel and the 12% chromium stainless steels were the most corrosion-resistant. The corrosion rate of 0.5% molybdenum and 1% chromium steels compared favourably with that of steels containing 5% of chromium. Non-ferrous materials were less corrosion-resistant in high-temperature steam than were high-alloy ferrous materials. Materials which corroded rapidly at 593° corroded only slightly at 496°, and at this lower temperature there was little difference in the corrosion rates of plain carbon and alloy steels. Additional data for the relative resistance to corrosion by steam of unstressed specimens of various alloy steels at 538—982° are presented by G. A. Hawkins, J. T. Agnew, and H. L. Solberg.<sup>70</sup> All the steels tested, with the exception of very high-chromium-nickel alloys, show rapid corrosion beyond a limiting temperature which rises with increasing chromium content. The chromium content of a steel appears to be a major factor in controlling the amount of corrosion produced by high-temperature steam. Analyses of the scale layers formed in 500-hour tests at 816° and 943° on various chromium-molybdenum steels showed that chromium, silicon, and molybdenum are more highly concentrated in the dense, middle layer than in the porous, brittle, outer layer.

The effects of adding 0.5—2% of molybdenum to 12% chromium steel on its suitability for high-temperature corrosion-resistant service in oil refineries and steam-power systems have been studied.<sup>71</sup> Short-time tensile properties at high temperatures and Charpy impact tests at room temperature, -5°, and -30° are recorded, and the effects of ageing for up to 1500 hours at 480—850° are considered. Addition of 1% of molybdenum increases the tensile strength and has little effect on the Charpy impact strength; with more than 1% of molybdenum the  $\alpha \rightarrow \gamma$  transformation is so far depressed that the steels become coarse-grained and relatively brittle. The further addition of about 1.0% of silicon to steel containing 1% of molybdenum has little effect on the load to fracture in 1000 hours when tested in the annealed condition, although it reduces the strength of quenched and tempered specimens. It improves the resistance to scaling in air at above 650°, however, and may be advantageous in some service conditions.

<sup>69</sup> *Trans. Amer. Soc. Mech. Eng.*, 1944, 66, 277; B., 1944, I, 410.

<sup>70</sup> *Ibid.*, 291; B., 1944, I, 410.

<sup>71</sup> *Met. and Alloys*, 1943, 18, 55; B., 1945, I, 231.



# NON-FERROUS METALS.

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## ORES AND EXTRACTION.

IN the field of flotation a comprehensive paper has been published by R. S. Dean and P. M. Ambrose,<sup>1</sup> in which many observations are explained in terms of a general theory of the use of wetting agents, according to which there is a balance between two influences: (a) a tendency to clean and wet the mineral particles, and (b) a tendency to preserve or form a water-repellent coating on them and thereby favour attachment of air bubbles. The agents are typically compounds in which one end of the molecule is particularly hydrophilic, and the ions formed in water are still polar and become oriented at oil-water and air-water interfaces. The long hydrocarbon chain may go into the anion (as in sodium lauryl sulphate, sodium octyl sulphate, sulphation products of hydroxylated organic compounds, and condensation products of alkylolamines with fatty acids) or into the cation (as in laurylpyridinium iodide, quaternary ammonium compounds, amines, etc.). Test results on the flotation of a number of minerals are described and a bibliography is appended. A. F. Taggart and N. Arbiter<sup>2</sup> have correlated contact angle measurements and solubility data with the mechanism of collection of minerals by amine-type collectors; they proceed to interpret practical flotation results on the basis of the theory that a precipitate of amine salt containing the acid ion of the mineral is formed at the solid surface. S. A. Falconer and B. D. Crawford<sup>3</sup> describe the details of treatment for froth flotation of a number of non-sulphide minerals. The application of flotation methods in the recovery of copper from slimes has been discussed.<sup>4,5</sup>

A review of the mechanism of gold and silver winning by amalgamation has been published by D. R. Hudson<sup>6</sup>; the view is expressed that the native metals adhere to the mercury as a result of surface tension and not necessarily as a result of the formation of intermetallic compounds, although such compounds may be formed slowly by diffusion when contact is prolonged. A. C. McDonald<sup>7</sup> reports the results of a series of tests on the roasting of pyritic gold ore containing arsenic and antimony in a rotary kiln. From 95 to 97% of the arsenic, from 25 to 30% of

<sup>1</sup> U.S. Bur. Mines, 1944, Bull. 449; B., 1944, I, 414.

<sup>2</sup> Amer. Inst. Min. Met. Eng., 1944, Tech. Publ. 1685; B., 1944, I, 373.

<sup>3</sup> Ibid., 1945; B., 1945, I, 110.

<sup>4</sup> B. Du Faur, Chem. Eng. Min. Rev., 1943, 35, 188; B., 1945, I, 301.

<sup>5</sup> Anon., ibid., 1942, 35, 22; B., 1945, I, 301.

<sup>6</sup> Metallurgia, 1944, 29, 255, 299; B., 1945, I, 38.

<sup>7</sup> Chem. Eng. Min. Rev., 1942, 35, 24; B., 1945, I, 303.



the antimony, and from 92 to 96% of the sulphur were eliminated in the furnace; smelting of the clinker with calcium carbonate and lead oxide gave a lead bullion containing antimony 7, arsenic 0.55, copper 0.57%, and gold 6.9 oz. per ton from original material containing arsenic 15, antimony 1.5%, and gold 1.4 oz. per ton.

V. I. Demidov and V. V. Stender<sup>8</sup> have designed a process for extracting lead from rich oxide ores found in thin layers in districts with poor transportation and fuel supply. The crushed ore, containing cerussite, anglesite, and zinc ores, is heated with sodium chloride solution, and sulphuric acid is then added to convert lead carbonate into soluble lead sulphate; excessive amounts of sodium sulphate, which hinder the dissolution of lead, are removed by adding calcium chloride. The solution is filtered and on cooling deposits lead chloride; more lead is precipitated by means of sodium sulphide. The lead precipitates are reduced with coal and chalk or lime.

A description of a plant for the production of magnesium from dolomite by the ferro-silicon process is given in a paper by A. Mayer<sup>9</sup>; the capacity of the plant is about 14 tons of magnesium per day. The dolomite is calcined, mixed with ferro-silicon, and briquetted; the briquettes are charged into horizontal retorts and heated at 1165° under low pressure. The condensate of magnesium is deposited in a removable sleeve fixed to each retort. A further paper on this subject by W. M. Peirce, R. K. Waring, L. D. Fetterolf, and G. T. Mahler<sup>10</sup> describes the results of investigations in a pilot plant, particularly with regard to briquetting procedure. The influence of degree of vacuum, time in furnace, grade of ferro-silicon, and additions of calcium fluoride on the yield of magnesium was studied; the technical superiority of aluminium over ferro-silicon as a reducing agent was confirmed. Difficulties encountered through the collapse of retorts for magnesium distillation are discussed by F. B. Foley and E. I. Sebastian.<sup>11</sup> T. A. Dugan<sup>12</sup> has described the production of magnesium by the carbothermic process starting from a raw material of 96% magnesium oxide obtained from sea-water. The plant, which contains four 6000-kw. reduction furnace units, is briefly described. C. E. Nelson<sup>13</sup> has published a detailed account of refining and melting magnesium.

Two papers<sup>14,15</sup> have appeared reporting on the operation of the Bureau of Mines electrolytic manganese pilot plant at Boulder City, Nevada. The output has been more than 550,000 lb. of manganese. The crushed ore is reduced to manganous oxide by roasting, oil being added; the

<sup>8</sup> *J. Appl. Chem. Russ.*, 1944, 17, 445; B., 1945, I, 337.

<sup>9</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1670; B., 1945, I, 163.

<sup>10</sup> *Ibid.*, 1707; B., 1945, I, 163.

<sup>11</sup> *Ibid.*, 1709; B., 1944, I, 373.

<sup>12</sup> *Ibid.*, 1671; B., 1944, I, 373.

<sup>13</sup> *Ibid.*, 1708; B., 1945, I, 164.

<sup>14</sup> R. S. Dean, *ibid.*, 1721; B., 1945, I, 74.

<sup>15</sup> J. H. Jacobs, J. W. Hunter, W. H. Yarroll, P. E. Churchward, and R. G. Knickerbocker, *ibid.*, 1717; B., 1945, I, 163.



product is leached with spent electrolyte and the solution neutralised with ammonia and treated with hydrogen sulphide in a stainless steel mixer. Colloidal sulphides and residual arsenic and molybdenum are removed by adding ferrous sulphate, oxidising with air by agitation at pH 6.5—7.0, and filtering. The efficiency of the electrolytic process has been greatly improved, causing less deposition of manganese dioxide at the anode; the fraction of manganese deposited at the anode to that at the cathode has been reduced from 0.25 to 0.0075.

D. C. McLaren<sup>16</sup> has given a brief survey of crushing, grinding, table and magnetic concentration, jigging, and flotation methods of treating tungsten ores and described the tungsten plant of the Hollinger Consolidated Gold Mines Ltd., which treats 65 tons of ore per day containing about 0.3% of  $\text{WO}_3$ . Concentrating practice in the Wilkes Creek tungsten mine is described by R. D. Nevett.<sup>17</sup>

During the war years secondary metals have been of particular interest, and it was timely that a symposium on the subject should be held.<sup>18</sup> Papers were communicated by F. W. Willard, F. H. Wright, F. E. Blyven, R. Schmidt, L. S. Deitz, jun., J. S. Earle, C. S. Cole, W. Romanoff, G. L. Craig, G. E. Behr, L. S. Thomas, J. J. Bowman, and C. E. Nelson. They covered mainly the reclamation of copper, tin, lead, aluminium, and magnesium, but also dealt with problems of collection and segregation and with war-time changes in the secondary metals industry.

### PROPERTIES.

Advances in physical knowledge provide greater opportunities to investigate the real significance of the gross values of properties of metals obtained by the conventional tests. A contribution to the study of hardness has been made by A. C. Vivian<sup>19</sup> in a theoretical investigation of the stress-strain relations in the neighbourhood of a Brinell impression. It is shown that marked yielding of the metal occurs at some distance below the impression. Hardness is regarded as a strength exhibited in loading by local compressive loads which, by the induction of lateral stresses in opposition to the development of the lateral strains, result in the development of less axial strain (for any degree of axial stress) than would be expected from the true stress-strain curve of single uni-directional loading. The relation between hardness and ultimate tensile strength is discussed. The study of hardness has also been advanced by experimental work by R. F. Bishop, R. Hill, and N. F. Mott<sup>20</sup> in an investigation of the indentation of work-hardened and annealed copper by cylindrical punches with conical heads, varying the diameter and angle of the punch.

<sup>16</sup> *Chem. Eng. Min. Rev.*, 1943, **35**, 181; B., 1945, I, 303.

<sup>17</sup> *Ibid.*, 1944, **37**, 38; B., 1945, I, 303.

<sup>18</sup> *Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1642, 2, 3, 13, 22, 26, 36, 39, 43, 46, 56, 65, 69, 77; B., 1944, I, 373.

<sup>19</sup> *Phil. Mag.*, 1944, [vii], **35**, 765; B., 1945, I, 138.

<sup>20</sup> *Proc. Physical Soc.*, 1945, **57**, 147; B., 1945, I, 306.



A symposium on cohesive strength, opened by M. Gensamer,<sup>21</sup> shows clearly the complexity of this subject. According to D. J. McAdam, jun.,<sup>22</sup> the technical cohesive strength of a metal in any particular state cannot be represented by a single stress value but only by a diagram with the principal stresses as co-ordinates. In such a diagram each point on the boundary represents a technical cohesion limit and the technical cohesive strength comprises an infinite number of such limits, each representing fracture under a particular stress combination. P. W. Bridgman's contribution<sup>23</sup> concerns the connexion between problems of flow and fracture and emphasises the importance of stress history in relation to fracture. L. R. Jackson<sup>24</sup> advances the hypothesis that the capacity of a metal for plastic flow before rupture is dependent on the type of stress system applied, and that the absolute magnitude of the stresses is unimportant, provided they are large enough to produce continued flow. The "tri-axial stress ratio," which may be used to characterise the type of stress system, is defined.

A comprehensive survey of data on the mechanical properties, thermal expansion, and thermal and electrical conductivity of metals and alloys at normal, high, and low temperatures has been compiled by J. L. Everhart, W. E. Lindlief, J. Kanegis, P. G. Weissler, and F. Siegel<sup>25</sup>; there are 724 references. Measurements of linear expansion of the face-centred cubic metals copper, aluminium, and lead from  $-190^{\circ}$  to near their melting points have been made by J. W. Richards.<sup>26</sup> M. Cook and E. C. Larke<sup>27</sup> have investigated the fundamental compression characteristics of copper and established a technique for determining curves of true resistance to homogeneous deformation by compression. Results are recorded for a number of copper alloys including brasses, nickel-silver, cupro-nickel, aluminium bronze, and phosphor-bronze. E. R. Parker and E. A. Smith<sup>28</sup> have shown that when single-crystal or polycrystalline samples of copper are broken in tension at 100 ft. per second, the elongation is greater than that of specimens broken at slower speeds; in the single-crystal specimens the slip bands on the polished surfaces are more numerous in the bars broken at the higher speeds. E. R. Parker and C. F. Riisness<sup>29</sup> report that the creep strength at  $200^{\circ}$  of oxygen-free high-conductivity copper bars (0.16, 0.375, and 0.505 in. diameter) is not influenced by variations in grain size from 3 to 2000 grains per sq. mm. The small bars were considerably weaker, particularly at high stresses, but their strength was increased considerably when

<sup>21</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1782, 1.

<sup>22</sup> *Ibid.*, 5.

<sup>23</sup> *Ibid.*, 32.

<sup>24</sup> *Ibid.*, 59.

<sup>25</sup> *U.S. Bur. Stand.*, 1943, *Circ.* C.447; B., 1945, I, 306.

<sup>26</sup> *Trans. Amer. Soc. Met.*, 1942, 30, 326; B., 1945, I, 337.

<sup>27</sup> *J. Inst. Metals*, 1945, 71, 371; B., 1946, I, 70.

<sup>28</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1704; B., 1944, I, 372.

<sup>29</sup> *Ibid.*, 1690; B., 1944, I, 372.



plated with cadmium. The rate of work-hardening of certain copper-base (and silver-base) solid-solution alloys has been examined,<sup>30</sup> and it is shown that linear relations exist between the rate of work-hardening and lattice expansion when the solute and solvent are in the same period of the periodic table.

Continuing his studies of tin bronzes, W. T. Pell-Walpole<sup>31</sup> has examined the effects of furnace atmosphere, of gases present in melting crucibles, and of various oxidising and reducing treatments on the properties of 14% tin bronze cast under controlled conditions. Melting conditions which favour gas absorption cause gas unsoundness and tin sweat; oxidising conditions without efficient deoxidation before pouring cause unsoundness due to shrinkage and steam porosity. The best material is obtained only by the use of oxidising fluxes with efficient deoxidation before pouring. Annealing to absorb the  $\delta$  phase before rolling causes the porosity to increase, but this is only slight in melts produced under oxidising fluxes. W. T. Pell-Walpole<sup>32</sup> has also investigated the deoxidation of 14% tin bronze melted under an oxidising flux. Phosphorus is a fully effective deoxidant if sufficient is added to provide a residual content of 0.02% in the bronze. Deoxidation with aluminium yields bronze of higher density, but of inferior mechanical properties owing to entrapped oxide films. The oxidation and deoxidation of copper has been investigated by P. Bastien and L. Guillet, jun.,<sup>33</sup> using aluminium, magnesium, silicon, calcium, and phosphorus as deoxidising agents; complete deoxidation of copper containing 1.35% of oxygen was obtained with 5% of calcium or with 2.5% of 15% phosphor-copper. The control and removal of oxides of nickel and iron in copper has been discussed by R. Krulla.<sup>34</sup> M. B. Bever and C. F. Floe<sup>35</sup> report that the solubility of hydrogen in copper at one atmosphere pressure varies almost linearly from 5.73 c.c. per 100 g. at 1100° to 9.37 c.c. per 100 g. at 1300°; corresponding solubilities in tin are about 0.02 at 1000° and about 0.36 at 1300°. The solubility of hydrogen in copper-tin alloys decreases rapidly as tin is added up to the composition corresponding with  $\text{Cu}_3\text{Sn}$  and then slowly with further addition of tin. This observation is said to support the view that  $\text{Cu}_3\text{Sn}$  exists in the molten state.

The effect of lead on the tensile properties of manganese bronze has been studied by G. P. Halliwell.<sup>36</sup> A. H. Hesse, E. T. Myskowski, and B. M. Lorig<sup>37</sup> found that the amount of lead which could be added to manganese bronze without seriously impairing the mechanical properties depended on the copper-zinc ratio and the tin content. Tin was an

<sup>30</sup> J. H. Frye, jun., and C. P. Sun, *ibid.*, 1711; B., 1944, I, 374.

<sup>31</sup> *J. Inst. Metals*, 1945, 71, 267; B., 1946, I, 69.

<sup>32</sup> *Ibid.*, 37; B., 1946, I, 30.

<sup>33</sup> *Rev. Mét.*, 1943, 40, 3; B., 1945, I, 161.

<sup>34</sup> *Metallwirts.*, 1943, 22, 111; B., 1945, I, 162.

<sup>35</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1703; B., 1944, I, 373.

<sup>36</sup> *Trans. Amer. Found. Assoc.*, 1944, 51, 837; B., 1944, I, 411.

<sup>37</sup> *Ibid.*, 821.



effective inhibitor of dezincification; arsenic and phosphorus showed beneficial effects, whilst antimony was harmful.

The electrical resistivity of  $\alpha$ -solid solutions in the copper-zinc and copper-tin alloy series has been determined in annealed and hard-drawn specimens over the temperature range from  $14.3^{\circ}$  K. to room temperature.<sup>38</sup> R. S. French<sup>39</sup> has investigated the effects of time and temperature of annealing and of the amount of prior cold reduction on the grain size of 70/30 cartridge brass. E. Vaders, E. Lay, and J. Fankhänel<sup>40</sup> have indicated the possibility of considerably improving the properties of alloys containing about 50% of copper by addition of manganese. In a series of brasses they have examined the effects on the mechanical properties of introducing 3—5% of manganese with and without small additions of aluminium, iron, silicon, or lead. Representative properties obtained in the hot-worked or annealed condition are: ultimate tensile strength 65 kg. per sq. mm., elongation 24%, Brinell hardness 135. J. R. Long and T. R. Graham<sup>41</sup> have studied the physical and working characteristics of an alloy containing copper 65, manganese 10, and zinc 25% as a possible substitute for 70/30 brass for cartridge cases. The grain size is finer than that of brass and the alloy is harder and rather less ductile, work-hardens more rapidly, and has a higher softening temperature. The alloy is subject to season cracking, but its hot-rolling characteristics are less affected by lead and antimony than are those of brass. H. L. Burghoff and J. S. Porter<sup>42</sup> have shown that in annealed 70/30 brass wire the preferential orientation of the [111] fibre axis is less intense when intermediate annealing is carried out at  $593^{\circ}$  than at  $427^{\circ}$ , but is intensified by severe final reductions and by raising the temperature of the final anneal.

J. C. Chaston<sup>43</sup> has observed that when oxygen-free silver containing 0.01—0.02% of metallic impurities is annealed in the air a zone of fine grains is formed just below the surface, whilst in the interior recrystallisation and grain growth proceed normally; this zone is not formed on annealing in vacuum or in hydrogen. When oxygen-bearing silver containing these traces of impurities is heated in hydrogen the metal becomes embrittled. As neither grain growth restraint nor hydrogen embrittlement is observed in very pure silver, it is suggested that the effects mentioned above may be ascribed to distributed particles of metallic oxides formed by internal oxidation. Alloys of silver with small amounts of aluminium or zinc are hardened for a small distance below the surface when annealed in air, presumably by a similar mechanism. R. M. Treco and J. H. Frye, jun.,<sup>44</sup> report that no measur-

<sup>38</sup> H. A. Fairbank, *Physical Rev.*, 1944, [ii], **66**, 274; A., 1945, I, 118.

<sup>39</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1673; B., 1944, I, 372.

<sup>40</sup> *Metallwirts.*, 1944, **23**, 81; B., 1945, I, 301.

<sup>41</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1705; B., 1945, I, 73.

<sup>42</sup> *Ibid.*, 1944, I, 372.

<sup>43</sup> *J. Inst. Metals*, 1945, **71**, 23; B., 1946, I, 32.

<sup>44</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1768; B., 1945, I, 269.



able increase in Meyer hardness could be detected when 0.53 at.-% of antimony was added to silver, but at higher concentrations there was a marked hardening effect, increasing as a linear function of the amount of antimony added. The density and plasticity of silver amalgams have been studied by D. R. Hudson.<sup>45</sup>

E. von Rajakovics<sup>46</sup> reports a number of fatigue tests in alternating bending, alternating torsion, and tension-compression on alloys of aluminium with magnesium, manganese, magnesium plus manganese, copper plus magnesium, copper plus nickel, and magnesium plus silicon respectively, in different conditions and with varying surface finish. The properties and annealing of rolled aluminium-magnesium alloys have been studied by W. Lott.<sup>47</sup> The properties of aluminium-magnesium-calcium alloys have been investigated by T. A. Badaeva and F. I. Schamrai<sup>48</sup> and the same authors<sup>49</sup> have made a study of ternary alloys of aluminium with magnesium and lithium.

A study of zinc-containing silumins (zinc 8—15, silicon 5—8, copper < 0.6, magnesium < 0.2, manganese 0.4—0.8%, and the balance aluminium) has been made by A. A. Botschvar, A. A. Vaschtschenko, S. G. Glazunov, O. S. Shadaeva, A. M. Korolkov, K. I. Portnoi, E. M. Savitzki, and Z. A. Sviderskaja.<sup>50</sup> The density of the alloys is 2.94—2.97, heat capacity 0.211, thermal expansion between 0° and 250°  $24.4 \times 10^{-6}$ , liquidus temperature 575°, solidus temperature 545°; ultimate tensile strength increases from 16 kg. per sq. mm. to 25 kg. per sq. mm. with increase of zinc content and is not raised by annealing at 100—300°. The castability of the alloys is good and they can be welded without loss of strength. The effect of additions of copper, magnesium, iron, and manganese to alloys of this type has been studied by S. G. Glazunov.<sup>51</sup>

E. A. G. Liddiard and W. A. Baker<sup>52</sup> have investigated the distribution of porosity and unsoundness in magnesium alloy castings solidified under controlled conditions, with special reference to the effect of gas and methods for its elimination. The conditions necessary for the production of sound castings are described. F. A. Fox<sup>53</sup> has studied the properties of magnesium-aluminium-zinc alloys (containing up to 10% of aluminium and 6% of zinc), especially as regards the incidence of micro-porosity. The higher zinc alloys are less satisfactory than those of lower zinc content and the mechanical properties of all alloys suffer more or less severely from the presence of micro-porosity.

<sup>45</sup> *Physical Rev.*, 1944, [ii], **65**, 247; A., 1944, I, 276.

<sup>46</sup> *Metallwirts.*, 1943, **22**, 225; B., 1945, I, 234.

<sup>47</sup> *Ibid.*, 1944, **23**, 135; B., 1945, I, 305.

<sup>48</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1944, 182; B., 1945, I, 75.

<sup>49</sup> *J. Appl. Chem. Russ.*, 1944, **17**, 230; B., 1945, I, 304.

<sup>50</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1943, Part 9/10, 3; B., 1945, I, 39.

<sup>51</sup> *Ibid.*, Part 11/12, 78; B., 1945, I, 39.

<sup>52</sup> *Inst. Brit. Foundrymen*, June, 1945, Paper 823; B., 1945, I, 269.

<sup>53</sup> *J. Inst. Metals*, 1945, **71**, 415; B., 1946, I, 72.



A study of soft soldering from a new viewpoint has been made by L. G. Earle<sup>54</sup> with the aid of a new apparatus called the Kollagraph. The importance of the time factor in the quantitative assessment of jointing capacity of a soldering system is emphasised, and it is shown that jointing capacity may be analysed into two independent characteristics of the soldering system; its time/temperature wetting characteristic and its interfacial tension characteristic. The minimum effective wetting temperature (M.E.W.T.) is defined as the lowest temperature at which the soldering system under review produces instantaneous wetting under the conditions of test, and has been measured for a number of solders, fluxes, and basis stocks. The results show clearly that the idea of joint-forming capacity or penetrative power cannot properly be applied to a solder alone, but is a feature of the system solder-flux-stock. The ease of soldering of such systems has been compared quantitatively by means of the M.E.W.T. and the penetrative power of the system measured in terms of the interfacial tension between the flux-covered solder and the fluxed stock. Different types of solder are selective in their reaction to both stock and flux.

#### CONSTITUTION AND STRUCTURE.

G. V. Raynor and (Miss) K. Little<sup>55</sup> have re-determined the solid solubility curve for chromium in aluminium between the peritectic temperature and 350°, using micrographic methods. The composition of the phase which enters into equilibrium with the primary solid solution has been accurately established as  $\text{CrAl}_7$ . The same authors<sup>56</sup> have also examined the constitution of the aluminium-rich aluminium-chromium-manganese alloys. At temperatures above 590° the phases in equilibrium in the solid alloys are  $\alpha$ ,  $\text{MnAl}_6$ , and  $\theta$ ; below 590° the ternary compound  $G$  also appears in equilibrium with the  $\alpha$  phase. Equilibrium is attained very slowly in these alloys. At 680° the aluminium-rich liquid enters into equilibrium with  $\text{MnAl}_6$  and the  $\theta$  phase and also with an  $\eta$  phase which is based on the binary aluminium-chromium  $\eta$  phase. The  $\alpha$ ,  $\text{MnAl}_6$ , and  $\theta$  phases are formed by a ternary eutectic reaction at 657.7°. The  $\eta$  phase remains in equilibrium with the aluminium-rich liquid almost down to the eutectic temperature and crystallises as a primary constituent over a wide composition range. The solubility of manganese in solid aluminium above 500° has been determined by microscopical methods by E. Butchers and W. Hume-Rothery<sup>57</sup>; the maximum solubility at the 658.5° eutectic horizontal is 1.32% of manganese. V. I. Micheeva and O. N. Kriukova<sup>58</sup> have shown that the ternary  $T$  phase in aluminium-magnesium-zinc alloys at the

<sup>54</sup> *J. Inst. Metals*, 1945, 71, 45; B., 1946, I, 32.

<sup>55</sup> *Ibid.*, 481; A., 1946, I, 80.

<sup>56</sup> *Ibid.*, 493; A., 1946, I, 116.

<sup>57</sup> *Ibid.*, 87; A., 1946, I, 18.

<sup>58</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1944, 296; A., 1945, I, 242.



crystallising point contains the compound  $\text{Al}_2\text{Mg}_3\text{Zn}_3$ ; at lower temperatures the electrical resistance and its temperature coefficient indicate the presence of  $\text{Al}_3\text{Mg}_4\text{Zn}_3$ . The aluminium-rich corner of the system aluminium-iron-nickel has been examined by A. Schrader and H. Hanemann<sup>59</sup>; the constituents observed were the aluminium-rich solid solution,  $\text{FeAl}_3$ ,  $\text{NiAl}_3$ , and the ternary phase  $T$  which extends at  $620^\circ$  from 18% of iron and 13.3% of nickel to 8.1% of iron and 23% of nickel. The binary aluminium- $\text{NiAl}_3$  eutectic temperature is given as  $641^\circ$  and that of the binary aluminium- $\text{FeAl}_3$  eutectic as  $655^\circ$ . E. Butchers and W. Hume-Rothery<sup>60</sup> have determined the solidus and liquidus curves for the  $\alpha$ -solid solution of the aluminium-magnesium system and for a wide range of alloy compositions in the system aluminium-zinc. The results are discussed from the thermodynamic viewpoint. The investigation has been extended to the determination of liquidus isothermals at  $630^\circ$  and  $550^\circ$  for the  $\alpha$ -solid solution of the ternary system aluminium-magnesium-zinc; the solidus isothermals of aluminium-rich alloys have also been determined for the ternary systems aluminium-magnesium-zinc, aluminium-magnesium-manganese, and aluminium-manganese-zinc, and for the quaternary system aluminium-magnesium-manganese-zinc.

G. Edmunds<sup>61</sup> has described technique for determination of the liquidus of alloys subject to super-cooling and recorded data for zinc-iron alloys from  $422^\circ$  to  $607^\circ$ , for zinc-copper alloys from  $427^\circ$  to  $594^\circ$ , and for zinc-manganese alloys from  $440^\circ$  to  $800^\circ$ . The composition of the zinc-iron eutectic is placed at 0.012% iron. E. A. Anderson, E. J. Boyle, and P. W. Ramsey<sup>62</sup> state that a zinc-titanium eutectic occurs with 0.12% of titanium at  $418.5^\circ$  and the solid solubility of titanium in zinc is 0.007—0.015% at  $300^\circ$ . The addition of 0.05—0.23% of titanium to zinc causes grain refinement. The indium-zinc system has been examined by F. N. Rhines and A. H. Grobe.<sup>63</sup> There is a eutectic at  $143.5^\circ$  containing 2.8% of zinc. The maximum solubility of zinc in indium is 1.2% and that of indium in zinc is 0.2%.

W. T. Pell-Walpole<sup>64</sup> has described some non-equilibrium structures in chill-cast tin-antimony-cadmium alloys and noted their effects on mechanical properties. Alloys of this series containing metastable suppressed  $\beta$  have high mechanical properties in the as-cast form, but do not retain these properties on ageing at room temperature. Alloys containing 9—14% of antimony and 1.5—10% of cadmium have much higher mechanical properties in the chill-cast condition, when they contain metastable  $\text{SbSn}$ , than in stable equilibrium, when  $\text{SbSn}$  is

<sup>59</sup> *Aluminium*, 1945, 25, 339.

<sup>60</sup> *J. Inst. Metals*, 1945, 71, 291; A., 1946, I, 80.

<sup>61</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1686; A., 1945, I, 54.

<sup>62</sup> *Ibid.*, 1687; A., 1944, I, 243.

<sup>63</sup> *Ibid.*, 1682; A., 1944, I, 244.

<sup>64</sup> *J. Inst. Metals*, 1945, 71, 441; B., 1946, I, 71.



replaced by CdSb. Chill-cast alloys containing 7–10% of antimony and 0.5–2% of cadmium can be temper-hardened at 140°. The significance of these properties in relation to the choice of alloys for bearing metals is discussed. In the ternary system bismuth–lead–zinc, S. D. Muzaffar and R. Chand<sup>65</sup> have shown that a ternary eutectic (m.p. 124°) is formed with bismuth 55, lead 43, zinc 2%. A separate liquid layer is formed when more than 10% of zinc is added to miscible binary alloys of bismuth and lead.

The transition temperatures of manganese have been determined by R. S. Dean, J. R. Long, T. R. Graham, E. V. Potter, and E. T. Hayes<sup>66</sup> with the following results:  $\delta \rightleftharpoons \gamma$  at  $1133^\circ \pm 3^\circ$ ,  $\gamma \rightleftharpoons \beta$  at  $1091^\circ \pm 3^\circ$ ,  $\beta \rightleftharpoons \alpha$  at  $705^\circ \pm 5^\circ$ . The constitution of the manganese–copper series of alloys was also studied: at high temperatures copper and  $\gamma$ -manganese form a continuous series of solid solutions, but at lower temperatures alloys containing more than 25% of manganese precipitate  $\alpha$ - or  $\beta$ -manganese; the  $\gamma \rightleftharpoons \beta$  transformation is lowered from 1091° to 705° at 70% of manganese and entirely suppressed at lower manganese contents; the  $\beta \rightleftharpoons \alpha$  transformation remains constant at 705° with 100–70% of manganese, but at lower manganese contents  $\alpha$ -manganese is precipitated directly from the  $\gamma$ -solid solution. Dissolution of manganese in copper increases the lattice spacing of the latter to a peak value at 65% of manganese. With more than 82% of manganese the crystal structure changes from face-centred cubic to face-centred tetragonal. The binary copper–manganese system has also been studied by X-ray methods by L. D. Ellsworth and F. C. Blake.<sup>67</sup>

Some light on the existence of intermetallic compounds in the molten state has been shed by the work of E. Heymann, R. J. L. Martin, and M. F. R. Mulcahy<sup>68</sup> by studying the deviations from Raoult's law of distribution equilibria between molten metals and molten salts. The curve for the distribution of sodium between molten cadmium and molten sodium bromide shows positive deviations, implying that the compounds NaCd and NaCd<sub>5</sub> are unstable at the experimental temperature (780°). Strong negative deviations in the curve for lead and sodium bromide indicate the existence of stable compounds Na<sub>3</sub>Pb<sub>8</sub>, Na<sub>2</sub>Pb, NaPb, and NaPb<sub>5</sub> at that temperature. Evidence of the existence of the intermetallic compound CdSb in the molten state is also given.

#### HEAT-TREATMENT AND PRECIPITATION-HARDENING.

The mechanism of precipitation in crystals of metallic solid solutions has been studied by A. Guinier for the systems aluminium–copper and aluminium–silver<sup>69</sup> and for aluminium–zinc alloys<sup>70</sup>; X-ray diffraction

<sup>65</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1374; A., 1945, I, 22.

<sup>66</sup> *Amer. Soc. Metals, Preprint* 9, 1944.

<sup>67</sup> *J. Appl. Physics*, 1944, **15**, 507; A., 1945, I, 276.

<sup>68</sup> *J. Physical Chem.*, 1943, **47**, 473; A., 1944, I, 63.

<sup>69</sup> *J. Phys. Radium*, 1942, [viii], **3**, 124; A., 1945, I, 92.

<sup>70</sup> *Métaux, Corrosion-Usure*, 1943, **18**, 209.



studies during the process showed that the solute atoms assemble into nuclei before precipitation begins. In aluminium–zinc alloys J. Herenguel and G. Chaudron<sup>71</sup> report that solid solutions show considerable structural hardening after relatively short annealing at the softening temperature; small amounts of magnesium or iron accelerate the hardening.

Investigations on age-hardening phenomena in aluminium–copper–magnesium alloys have been published by K. L. Dreyer.<sup>72</sup> An increase in magnesium content from 0.8 to 1.3% or of silicon from 0.2 to 1.2% reduces the amount of softening in the region of 200° whether the alloys have previously been age-hardened or not; the rate of subsequent room-temperature age-hardening is also reduced. K. L. Dreyer and M. Hansen<sup>73</sup> have also examined the effect of varying the magnesium content and amount of silicon addition to age-hardening aluminium–copper–magnesium alloys containing 2% of copper. Time/hardness curves of an aluminium alloy containing copper 2.6, magnesium 1.8, manganese 0.65, iron 0.4, silicon 0.95, and titanium 0.17% have been determined at temperatures between 20° and 500°; maximum hardness is attained after 6 hours at 200°. T. A. Badaeva and F. I. Schamrai<sup>74</sup> report that the addition of calcium to aluminium–magnesium alloys increases the effectiveness of artificial ageing so long as the magnesium–calcium ratio does not exceed 13:1. Data are recorded for aluminium–magnesium alloys containing 0.2–1.0% of magnesium and for ternary alloys containing 0.05–0.65% of magnesium and 0.003–0.05% of calcium, aged at 175° and at 200°. A. M. Korolkov and N. V. Barischnikova<sup>75</sup> have studied the effect of time of heat-treatment on the tensile properties of a cast aluminium alloy containing silicon 10.90, iron 0.64, manganese 0.40, and magnesium 0.30%.

R. S. Dean, J. R. Long, T. R. Graham, and C. W. Matthews<sup>76</sup> have studied copper–manganese–nickel alloys (containing 22–24% of nickel and manganese, respectively) as a substitute for beryllium–copper. Response to age-hardening treatment was good; reproducible hardness and other properties were obtained by quenching from 650° followed by ageing at 350–450° for periods up to 24 hours. Ageing occurred more rapidly from the cold-worked condition than from the solution-treated state. Alloys hardened from the solution-treated state showed the highest elongation after ageing at 400°, whilst in general the maximum tensile properties for a given hardness were obtained by ageing at 450°. Wide ranges of physical properties could be obtained by suitable variation of heat-treatment.

<sup>71</sup> *Compt. rend.*, 1943, 216, 687; B., 1944, I, 414.

<sup>72</sup> *Metallwirts.*, 1943, 22, 43; B., 1945, I, 164.

<sup>73</sup> *Z. Metallk.*, 1943, 35, 137.

<sup>74</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 394; B., 1945, I, 75.

<sup>75</sup> *Ibid.*, 57; B., 1945, I, 39.

<sup>76</sup> *Amer. Soc. Metals, Preprint* 11, 1944.



## CORROSION AND PROTECTION.

The considerable interest now being taken in the study of stress-corrosion is reflected in the symposium held in November, 1944, by the American Society for Testing Materials and the American Institute of Mining and Metallurgical Engineers. Papers were read by E. H. Dix, jun., H. Brown, G. Edmunds, E. A. Anderson, R. K. Waring, H. Gisser, J. W. Mitchell, H. Rosenthal, J. Mazia, G. Sachs, G. Espey, S. N. Clark, T. A. Read, J. B. Reed, G. R. Gohn, S. M. Arnold, C. W. George, B. Chalmers, R. B. Mears, R. H. Brown, F. A. Champion, and B. C. Madden, jun.<sup>77</sup> The papers dealt particularly with the stress-corrosion of brass and of aluminium alloys, and there was also discussion of the theory of the process, methods of testing, and the significance of the results. Some confusion exists between this and other types of stress failure and between corrosion-fatigue and stress-corrosion. In most cases the failure appears to occur by an electrochemical mechanism, but tensile stress must be present for cracking to occur, its effect being to open the crevices once corrosion has commenced. The type of corrosion involved is localised either at grain boundaries or at slip planes which are anodic to the surrounding metal in certain corroding environments. Preventive methods include low-temperature annealing, control of precipitation, provision of protective surface films and coatings, and suitable alloying. H. Rosenthal and A. L. Jamieson<sup>78</sup> have shown that stress-corrosion cracking occurs in 70/30 brass when stressed specimens are suspended in moist air containing vapours of various organic amines. A contribution to the technique of stress-corrosion testing has been made by W. D. Robertson,<sup>79</sup> who also describes apparatus for the purpose.

The atmospheric oxidation of aluminium, magnesium, and their binary alloys has been studied by an electron-diffraction method by L. de Brouckère.<sup>80</sup> The film formed on aluminium heated between 400° and 500° for a comparatively long time consists of  $\gamma$ - $\text{Al}_2\text{O}_3$ , but a film of amorphous  $\text{Al}_2\text{O}_3$  is formed by rapid heating at 500°. The film which forms on aluminium at room temperature is less than 100 Å. thick. Comparatively thick films are formed on magnesium or aluminium containing 35% of magnesium after any treatment. When produced at room temperature the film is amorphous, but becomes crystalline after heating above 200°. In the alloys the film may contain both  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ , but the black film sometimes formed is shown to consist of  $\text{MgO}$ . O. Kubaschewski<sup>81</sup> has studied the rate of oxidation of alloys of platinum and gold with copper and nickel respectively at high temperatures in air; in every case an impervious layer of nickel oxide or cuprous oxide is formed on the surface. J. A. Hedvall and G. Ekwall<sup>82</sup> have

<sup>77</sup> A.S.T.M.-A.I.M.E. Symposium on Stress-Corrosion Cracking, Preprint 7, 1944.

<sup>78</sup> Amer. Inst. Min. Met. Eng., 1944, Tech. Publ. 1660; B., 1944, I, 373.

<sup>79</sup> Canad. J. Res., 1945, 23, A, 263; C., 1945, 300.

<sup>80</sup> J. Inst. Metals, 1945, 71, 131; B., 1946, I, 35.

<sup>81</sup> Z. Elektrochem., 1943, 49, 446; A., 1945, I, 160.

<sup>82</sup> Arkiv Kemi, Min., Geol., 1944, 18, A, No. 11; A., 1944, I, 287.



shown that the rate of tarnishing of copper by iodine is increased by supersonic vibrations.

In the report for 1944 reference was made to the corrosive effect of domestic water supplies on galvanised iron and on lead; further contributions to this important subject have appeared. Some problems of corrosion in hot-water systems, with particular reference to galvanised iron, are discussed by A. H. Ulbrich<sup>83</sup> and by W. A. Mayhan.<sup>84</sup> L. W. Haase<sup>85</sup> has described the characteristics of Norwegian water supplies and the corrosive effects caused by cold and hot water containing carbon dioxide and non-volatile acids. E. P. Polushkin and H. L. Shuldener<sup>86</sup> have published the results of a microscopical examination of brass pipes removed from buildings in New York after periods of service of up to 20 years in hot-water systems; the rate of general corrosion was small and most of the destruction was due to local corrosion. It appeared that grain size had no influence on corrosion, but local attack was traced to surface defects and residual stresses.

Measurements by G. E. Coates<sup>87</sup> of the rate of corrosion of magnesium in dilute acids have shown that there is a linear proportionality between the logarithm of the corrosion rate and the logarithm of the acid concentration. Concentration-polarisation phenomena have also been studied and are said to confirm the view that the acid corrosion of magnesium occurs by way of a diffusion-control mechanism. The same author<sup>88</sup> has also found that the rate of dissolution of magnesium in deuterochloric acid in 0.07—0.1N. solutions is identical with that in hydrochloric acid, but at lower concentrations the rate in deuterochloric is less than in hydrochloric acid. The influence of pH on the rate of corrosion of magnesium has been studied by G. V. Akimov and I. L. Rozenfeld.<sup>89</sup> Below pH 3 there is a sharp increase in corrosion rate, between pH 3 and pH 11 the rate of corrosion decreases gradually, and at values of pH greater than 11 protective films are formed and the rate of corrosion falls abruptly.

The corrosion of magnesium-aluminium alloys (containing 0.50% of zinc and 0.30—0.20% of manganese) in the atmosphere and when immersed in 3% sodium chloride solutions has been investigated by F. A. Fox and C. J. Bushrod<sup>90</sup> with special reference to the influence of manganese content and of small amounts of iron (0.001—0.024%). Within the given range of manganese, variations in the iron content have no appreciable effect on the results of either atmospheric tests or immersion tests, whether in the as-cast or heat-treated condition. Specimens

<sup>83</sup> *Proc. Ann. Arkansas Water & Sewage Conf.*, 1944, **14**, 72.

<sup>84</sup> *Ibid.*, 78.

<sup>85</sup> *Korros. u. Metallschutz*, 1942, **18**, 145; B., 1945, I, 265.

<sup>86</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1742; B., 1945, I, 267.

<sup>87</sup> *J. Inst. Metals*, 1945, **71**, 457; B., 1946, I, 109.

<sup>88</sup> *J.C.S.*, 1945, 470; A., 1945, I, 276.

<sup>89</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **44**, 193; A., 1945, I, 119.

<sup>90</sup> *J. Inst. Metals*, 1945, **71**, 255; B., 1946, I, 109.



which had received a solution heat-treatment were found to corrode more rapidly when tested by complete immersion, although under atmospheric exposure the structural state of the alloy did not influence corrosion-resistance. The behaviour of a number of magnesium alloys in soils has been studied by W. Wiederholt.<sup>91</sup> The corrosiveness of the soils was in the order chalky > loamy > peaty > sandy. Most attack was caused by chloride and sulphate ions and in basic soils the formation of magnesium hydroxide caused a cementing of soil to metal. Magnesium-manganese alloys were less attacked than magnesium-aluminium alloys.

Some relations between corrosion and fouling of copper, nickel, and copper-nickel alloys in natural sea-water have been determined by F. L. LaQue and W. A. Clapp.<sup>92</sup> Copper was not fouled, but nickel and the alloys containing more than 30–40% of nickel were fouled appreciably. Fouling was prevented when the amount of corrosion was sufficient to liberate more than 7.0 mg. of copper per sq. dm. per day.

Considerable use is now being made of passivation treatments, particularly for zinc surfaces. Some useful reviews of these processes have appeared.<sup>93,94</sup> The Cronak process in particular has been described and investigated by S. G. Clarke and J. F. Andrew.<sup>95</sup> They show that heating the film even in hot water reduces its protective value; the freshly prepared film is hydrated and its dehydration on heating appears to cause increased permeability. The normal film is 0.00001–0.00002 in. thick and gives good protection against moisture or salt spray.

It has been shown by E. S. Hedges and L. A. Jordan<sup>96</sup> that electrodeposits of tin 0.000008 and 0.00003 in. thick on steel form an excellent base for paints, providing greatly increased corrosion-resistance. Standard accelerated corrosion tests were made with 12 different paints, including linseed oil paints, nitrocellulose lacquer, stoving paints, and air-drying japans. The best treatment was found to be 0.00003 in. of tin, electrodeposited from the sodium stannate bath and further protected by a film applied by immersion in an alkaline phosphate-chromate solution. The effectiveness of thin undercoats of electrodeposited tin in increasing the corrosion-resistance of steel plated with zinc, cadmium, or nickel has been demonstrated by S. Wernick.<sup>97</sup>

<sup>91</sup> *Korros. u. Metallschutz.*, 1942, **19**, 289; B., 1945, I, 304.

<sup>92</sup> *Trans. Electrochem. Soc.*, 1945, **87**, Preprint 15, 165; B., 1945, I, 268.

<sup>93</sup> K. Voss, *Metallwirts.*, 1942, **21**, 754; B., 1945, I, 131.

<sup>94</sup> F. Taylor, *Metallurgia*, 1944, **30**, 275; B., 1944, I, 412.

<sup>95</sup> *J. Electrodep. Tech. Soc.*, 1945, **20**, 119; B., 1945, I, 336.

<sup>96</sup> *J. Iron & Steel Inst.*, July, 1945, **152**, 429P; B., 1945, I, 336.

<sup>97</sup> *J. Electrodep. Tech. Soc.*, 1944, **20**, 47; B., 1945, I, 194.



# ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES.

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THE volume of literature relating to the advancement of these industries published during the period under review, while still well below the pre-war level, has shown a marked increase as compared with the preceding year. For reasons of security the results of much of the research and development conducted during the war years have not hitherto been made public, but there are growing signs of relaxation and more information is beginning to find its way into the technical press.

Discussing the possible development of these industries in this country, A. G. Robiette<sup>1</sup> remarks that before the war we imported the bulk of our electrochemical and electrometallurgical products, or in other words we imported the equivalent of vast quantities of water power. In connexion with the proposed development of hydro-electric power in the Scottish Highlands he estimates that the establishment of these industries would create a demand for 231,500 kva., representing a consumption of about 1,600,000 kw.-hr. per annum based on 7500 working hours per annum and an average power factor of 0.9. This is regarded as a conservative estimate, and allowing for expansion it is thought that the full demand would approach half the total power which according to the Cooper Report will become available.

As regards recent progress the development of the sulphamate type of electrolyte both for the electrodeposition of metals and for anodising and of the fluoborate type of plating bath is noteworthy. Alloy plating continues to make headway while considerable interest is being revived in the deposition of bright plate. There is still much to be learnt of the mechanism of bright plating, however, and the immediate need for a thorough investigation of the subject has recently been emphasised.<sup>2</sup>

## ELECTROLYTIC PROCESSES.

### EXTRACTION, REFINING, PLATING, SURFACE TREATMENT, AND ELECTRODE REACTIONS OF METALS.

*Aluminium.*—Recent work on the rapid production of anodic films on aluminium-base alloys with particular reference to developments in the U.S.S.R. is described by E. E. Halls.<sup>3</sup> Using the sulphuric acid process, by making appropriate adjustments in the concentration of the bath, working temperature, and current density, it is possible to reduce

<sup>1</sup> *Metal Treatment*, 1945, 12, No. 42, 116.

<sup>2</sup> *Proc. Electrochem. Soc.*, 1944, 86, 33.

<sup>3</sup> *Metallurgia*, 1944, 30, 271; B., 1944, I, 414.



the time of treatment from 20 to 10 minutes. The advantages and applications of the Bengough-Stuart chromic acid anodising process are outlined by W. W. Moss and L. G. Tubbs, jun.,<sup>4</sup> who publish charts giving the pH of these solutions at 25° and the consumption of chromic acid in the anodising of Alclad 24 ST, and the alloys 17 ST and 24 ST. Tables giving the characteristics of baths working at 35° and 40 volts for various maintained pH values are appended, and the properties of coatings produced on Alclad by treatment under these conditions in a bath containing 100 g. of chromic acid per litre are discussed. In view of the interest taken in recent years in the deposition of metals from solutions containing sulphamic acid it is noteworthy that R. Piontelli<sup>5</sup> now claims that sulphamic acid solutions can be used as a substitute for the sulphuric acid bath for anodising aluminium; the main difference is that the new bath requires to be operated at a lower current density. In order to increase the protection afforded by the film produced on aluminium by anodic oxidation, N. D. Tomaschov and M. N. Tiukina<sup>6</sup> recommend treatment in a chromate solution maintained at a pH of 6—7. Adsorption of chromate by the film is accompanied by the formation of the compound  $\text{Al}_2\text{O}_3\cdot\text{CrO}_3$  and by a marked decrease in the porosity of the oxide resulting from hydration of the alumina.

J. D. Edwards and F. Keller<sup>7</sup> find that anodic films formed in boric acid electrolytes which exert no solvent action on the coating are non-porous, thin, and do not grow after they have once been formed. The coatings produced in the more usual baths containing sulphuric acid, oxalic acid, or chromic acid, on the other hand, all of which have an appreciable solvent action on the growing film, are characteristically porous. The authors have studied the mechanism of growth of the porous types of film and using the electron microscope have examined the size and spacing of the pores and the profile of the metal-oxide interface. Anodic coatings on aluminium have been claimed by some investigators to possess a crystalline structure and by others to be of an amorphous nature. C. S. Taylor, C. M. Tucker, and J. D. Edwards<sup>8</sup> have examined the structure of these coatings using X-ray diffraction methods and find that when the formation potential exceeds 100 volts the diffraction pattern corresponds with  $\gamma$ -alumina. Crystalline coatings were obtained with a wide variety of electrolytes, and it is therefore concluded that their formation is independent of the composition of the bath; it appears that a high electrostatic stress favours the formation of an ordered oxide lattice.

E. S. Bidgood and G. H. Kent<sup>9</sup> have investigated the practical problems involved in applying cataphoretic alundum coatings to radio tube parts,

<sup>4</sup> *Light Metals Age*, 1945, 3, No. 3, 10.

<sup>5</sup> *Korros. u. Metallschutz*, 1943, 19, 110.

<sup>6</sup> *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1944, 325; B., 1945, I, 305.

<sup>7</sup> *Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1710; B., 1944, I, 373.

<sup>8</sup> *Trans. Electrochem. Soc.*, 1945, 88, *Preprint* 9; B., 1946, I, 35.

<sup>9</sup> *Ibid.*, 87, *Preprint* 4; B., 1945, I, 169.



in particular to heaters made from tungsten wire. They favour the use of cataphoretic suspensions of alumina containing additions of aluminium and magnesium nitrates; the latter readily decompose when the coating is heated and the resulting oxides possess good electrical insulating properties and have a high heat-resistance. Moreover, the nitrates ionise and, therefore, increase the conductivity of the electrolyte, while they also aid in binding the deposited coating together as well as on to the basis metal.

Reference has previously been made to the work of R. G. Verdieck and L. F. Yntema on the use of aluminium as a reference electrode in studying the deposition potentials of metals from an aluminium chloride bath.<sup>10</sup> R. Wehrmann and L. F. Yntema<sup>11</sup> have now determined the deposition and decomposition potentials at 218° of aluminium, hydrogen, copper, and several other metals from fused baths containing aluminium bromide, an alkali bromide, and a metallic bromide or chloride, and of aluminium, silver, and mercury from similar baths containing aluminium chloride in place of bromide, using aluminium as the reference electrode. The deposition potentials vary from  $-0.02$  volt for aluminium at one end of the scale to  $+1.05$  volts for hydrogen at the other. The sum of the deposition and decomposition potentials for the aluminium bromide baths containing other metals is found to be  $1.61 \pm 0.04$  volts, which agrees with the value of 1.61 volts obtained for the decomposition potential in the absence of the other metals. R. G. Verdieck and L. F. Yntema<sup>11</sup> have supplemented this work by determining the deposition and decomposition potentials at 160° for a large number of metals from fused aluminium chloride-alkali chloride baths containing metallic chlorides and find a similar agreement between the sum of the two potentials and the value previously found for the decomposition potential of the bath in the absence of the second metal.

*Antimony.*—The nature of the cathodic polarisation of antimony with particular reference to the behaviour of this impurity in the electrolytic refining of copper has been studied by O. Esin.<sup>12</sup> He finds that the deposition of antimony from hydrochloric acid solutions is accompanied by concentration polarisation while from sulphuric acid solutions there is in addition a delayed discharge of the cation. To avoid the latter complication he recommends that approximately 10% of hydrochloric acid should be added to copper sulphate-sulphuric acid electrolytes and considers that in copper refining practice contamination of the cathodes by antimony need be only of secondary importance.

*Beryllium.*—Modern methods for the production of metallic beryllium are described by W. J. Kroll,<sup>13</sup> who states that the electrolysis of a fused

<sup>10</sup> See *Ann. Repts.*, 1942, 27, 243.

<sup>11</sup> *J. Physical Chem.*, 1944, 48, 259, 268; A., 1945, I, 67.

<sup>12</sup> *J. Appl. Chem. Russ.*, 1944, 17, 114; B., 1945, I, 233.

<sup>13</sup> *Metal Ind.*, 1945, 67, 148; U.S. Bur. Mines, 1945, *Inf. Circ.* 7326; B., 1946, I, 247.



chloride melt is the most usual method of extraction. The process suffers from several disadvantages, however, and notably is lengthy and deposits the metal as flakes in a form unsuitable for alloying without remelting. Kroll discusses possible future developments in the extraction of beryllium and in the preparation of its useful alloys direct from the ore.

*Bismuth.*—Developments in the recovery of bismuth from the anode slimes from copper, silver, tin, and lead refineries and from the manufacture of electrolytic white-lead are reviewed by A. G. Arend.<sup>14</sup> The general procedure is to melt the combined slimes, oxidise, sulphurise, and cast the reduced crude bismuth into rods, which are then electrolysed in a solution containing bismuth trichloride and hydrochloric acid using cathodes of a bismuth alloy.

*Cadmium.*—A warning of the health hazards involved in cadmium plating is given by P. A. Neal, L. T. Fairhall, and K. G. Soderberg.<sup>15</sup> They recommend that when operating solutions with insoluble steel anodes the plating tank should be ventilated as in chromium-plating practice, and stress the importance of refraining from inhaling salts containing cadmium when making up a new solution. Whenever cadmium has to be removed from a plated part it should be done so either by electrolysis or by chemical stripping. Heat should never be used as a means of removal and cadmium-bearing scrap should not be remelted except under thorough ventilation as the fumes from burning cadmium are highly toxic.

*Chromium.*—A. W. Hothersall<sup>16</sup> discusses the mechanical properties and adhesion strength of electrodeposited chromium and nickel in connexion with the building up of worn or under-size machine parts. He warns that coatings deposited on steel may impair its resistance to fatigue, and states that the hardness of the deposited metals is usually much greater than that of their as-cast or annealed counterparts. N. N. Sawin<sup>17</sup> reviews recent German practice in the deposition of hard chromium plate. A bath containing 200—400 g. of chromic acid per litre, and having a ratio of chromic acid to foreign acids, *e.g.*, sulphuric, hydrofluoric, hydrofluosilicic, or boric, of 100 : 1, operated at a temperature of 50—55° and current density of 40—60 amp. per sq. dm., is said to give the best results. Baths containing complex fluorides are particularly favoured, since compared with solutions containing sulphuric acid the cathode efficiency is approximately 50% higher. A dull, blue-grey deposit of hard chromium, according to A. Hirsch,<sup>18</sup> can be obtained from a standard chromium-plating bath containing 250 g. of chromic acid and 2.5 g. of sulphuric acid per litre by operating at 27—29° and a cathode current density of 16 amp. per sq. dm.

<sup>14</sup> *Ind. Chem.*, 1945, 21, 199; B., 1945, I, 194.

<sup>15</sup> *Iron Age*, 1944, 154, No. 14, 63.

<sup>16</sup> *Proc. Inst. Mech. Eng.*, 1945, 152, 8; B., 1945, I, 263.

<sup>17</sup> *Metal Ind.*, 1945, 66, 202.

<sup>18</sup> *Month. Rev. Amer. Electroplaters' Soc.*, 1945, 32, 119.



Electrodeposited hard chromium containing oil-retaining surface pores is being increasingly used as a means of reducing wear on engine cylinder liners, piston rings, rolls, etc. T. G. Coyle<sup>19</sup> states that in producing the porous plate the major controlling factors are the actual plating, the subsequent etching, and the finishing. For the plating a standard bath is usually employed having a sulphate ratio between 100/1 and 125/1. The concentration of chromic acid in the bath and cathode current density have little effect on the size of the crack pattern produced in the deposit, but the size increases with increase in the sulphate ratio and in temperature, the latter being the more critical factor. A temperature of 50° is usual when pin-point porosity is desired, and of 60° for producing the fissure type of porosity, both of which find application in practice. The porosity can be developed by chemical etching in an acid solution, by anodic etching in chromic acid, or by cathodic treatment in, for example, sulphuric or phosphoric acid; after etching a mechanical finishing operation is necessary to remove surface irregularities and leave the plate with a good running surface.

The uses of flash chromium plating, in which machine parts are coated with hard chromium not exceeding 0.001 in. in thickness deposited under carefully controlled conditions, are discussed by C. L. Tanner.<sup>20</sup> After plating, the work may if necessary be lapped or buffed, but is not ground to size. With reasonable care the plating thickness can be maintained within a tolerance of  $\pm 5\%$ . Flash plating is useful in reducing friction and improving resistance to corrosive attack. Plated tools do not readily pick up the metal being worked and chips tend to slide off the tool surface without transferring their heat thereto. G. E. Gardam<sup>21</sup> describes a method of producing machinable chromium plate having a hardness in the vicinity of 400 V.P.N. which can, however, be further softened by annealing at 150—250°. A suitable bath contains chromic acid, sulphuric acid, and iron, and is operated at 85° and 200 amp. per sq. ft. The presence in the bath of considerable quantities of trivalent metallic ions is necessary to increase the cathode efficiency at the high working temperature employed and helps to produce soft deposits over a wider range of current density. Examples of suitable trivalent ions are iron and chromium; aluminium is also efficacious and is best added to the bath as the hydroxide. The machinability of the deposits is improved by heat-treatment; deposits heat-treated at 200° remain brittle, but are readily machinable and turn like cast iron.

On prolonged electrolysis of a chromic acid solution using a platinum anode, E. Müller<sup>22</sup> has observed the formation thereon of a visible film of an insoluble yellow substance which he believes may be  $\text{Cr}(\text{OH})\text{CrO}_4$ . The development of the film affords an explanation of certain anomalies

<sup>19</sup> *Proc. Amer. Electroplaters' Soc.*, June, 1944, 20; cf. *Metal Ind.*, 1945, 67, 156.

<sup>20</sup> *Mech. Eng.*, 1944, 66, 726.

<sup>21</sup> *J. Electrodep. Tech. Soc.*, 1945, 20, 69; B., 1945, I, 195.

<sup>22</sup> *Z. Elektrochem.*, 1944, 50, 71; A., 1945, I, 145.



observed in the electrolysis of trivalent and hexavalent chromium solutions.

**Cobalt.**—Starting from a crude cobalt oxide cake which was converted into cobalt sulphate and electrolysed in a diaphragm cell using duriron anodes, N. Fedotov<sup>23</sup> has succeeded in obtaining cathode metal of purity 99.9%. The residual impurities are nickel and iron, and in order to keep these down to a minimum the excess of iron in the anolyte is removed by treatment with soda ash and the excess of nickel in the catholyte by treatment with dimethylglyoxime. The catholyte is regenerated by neutralising the spent anolyte with basic cobalt carbonate. The electrolysis is carried out at 50—55° and cathode current density of 5—6 amp. per sq. cm.; the current efficiency is between 65 and 70%.

**Copper.**—Y. Yao<sup>24</sup> has extended his studies on the electrolytic refining of copper to the examination of the behaviour of bismuth in copper sulphate electrolytes. He finds that increasing the chloride concentration of the solution up to about 15 mg. per litre decreases the tendency for the co-deposition of bismuth with the copper, the beneficial effect being greatest at a critical concentration of chloride. The chief function of the chloride ion is the precipitation of cuprous chloride and silver chloride, which carry down much of the bismuth into the anode slimes.

For the preparation of copper powder by electrodeposition, A. W. Hothersall and G. E. Gardam<sup>25</sup> recommend the use of a solution containing 50 g. of copper sulphate and 150 g. of sulphuric acid per litre, operated at 30° and a current density of 72 amp. per sq. ft., the anode area being greater than the cathode area and the inter-electrode spacing, which is governed by the method of removing the powder, being as small as possible. The powder may be efficiently washed by decantation, and after drying is of a gritty nature and flows readily; its apparent density is 1.3.

W. V. Sternberger and E. R. Fahy<sup>26</sup> claim that electrodeposited copper can be successfully used as a stop-off medium in the nitride hardening of steel and give details of the experimental nitriding of steel bushings protected in this way. To be effective the copper deposit must be dense and non-porous and should have a minimum thickness of 0.0004 in.

In a patent relating to the deposition of metals from sulphamate baths, M. E. Cupery<sup>27</sup> gives the composition and working conditions of a solution suitable for the deposition of copper. The bath is operated at room temperature and is claimed to produce good bright deposits. An interesting report on the deposition of metals from fluoborate solutions by H. Narcus,<sup>28</sup> to which further reference is made in the section of this report dealing with the deposition of alloys, mentions that concentrated solutions of the fluoborates of copper, iron, and other metals not hitherto

<sup>23</sup> *Trans. Electrochem. Soc.*, 1945, 87, Preprint 3; B., 1945, I, 194.

<sup>24</sup> *Ibid.*, Preprint 2; B., 1945, I, 193; cf. *Ann. Repts.*, 1944, 29, 226.

<sup>25</sup> *J. Electrodep. Tech. Soc.*, 1945, 20, 61; B., 1945, I, 193.

<sup>26</sup> *Metal Progr.*, 1945, 47, 278; B., 1945, I, 299.

<sup>27</sup> U.S.P. 2,318,592; B., 1945, I, 343.

<sup>28</sup> *Metal Finish.*, 1945, 43, 188, 242.



plated from this type of bath are now commercially available in the U.S.A., and warrant full investigation. Amongst other advantages fluoborate solutions are claimed to produce fine-grained deposits, to possess a relatively high throwing power, and to favour high anode and cathode efficiencies.

Referring to the black anodising of copper and brass, J. D. McLean and C. B. F. Young<sup>29</sup> describe a method of producing a deep black adherent coating of particular value in the optical field. The process involves anodic treatment at a temperature of 90—100° in a solution of sodium hydroxide, using steel or carbon cathodes.

*Indium.*—According to J. B. Mohler,<sup>30</sup> objections to the indium cyanide plating bath are difficulty of preparation, a tendency to decomposition, the necessity for ageing before use, and the fact that only insoluble anodes can be employed. He states that the first three of these disadvantages can be overcome by adding potassium hydroxide to the bath and recommends a solution containing 15—30 g. of indium per litre with potassium cyanide, potassium hydroxide, and dextrose. The solution favoured by W. M. Martz<sup>31</sup> contains indium in the form of borofluoride, silicofluoride, or trifluoride, and is operated with soluble indium anodes at a current density of 10—100 amp. per sq. ft.

*Iron.*—J. H. Bartlett<sup>32</sup> has applied the method of direct current transients to the study of phenomena in the cell  $\text{Fe}|\text{H}_2\text{SO}_4|\text{H}_2(\text{Pt})$  and adduces evidence that passive iron has on its surface an adsorbed layer which is unstable below a certain voltage, termed the activation potential. Between the passive region and the steady state a steady medial condition may intervene and appears to be related to the presence of the  $\text{HSO}_4^-$  ion. It is assumed that this ion reacts with ferrous ions to form a precipitate of which more can be held on the surface of the electrode the higher is the voltage within the range  $-0.3$  to  $+0.1$  volt with respect to the calomel cell.

*Lead.*—The influence of current density and concentration of the electrolyte on the quality of the cathode metal in the electrolytic refining of lead in sulphamic acid solutions has been investigated by V. V. Stender, E. A. Pavlov, and V. D. Budon.<sup>33</sup> Using an electrolyte containing 12% of lead as sulphamate together with free sulphuric acid, resorcinol, and glue, operated at a current density of 500 amp. per sq. m. with anodes containing 3.5% of bismuth, they have succeeded in depositing lead at a current efficiency of 99—100%. The cathode deposit contains not more than 0.006% of bismuth; 70% of the bismuth originally present in the anode is found in the anode sludge, which remains firmly adherent to the anodes.

<sup>29</sup> *Metal Finish.*, 1945, **43**, 247; cf. *Metal Ind.*, 1945, **67**, 118.

<sup>30</sup> *Iron Age*, 1945, **155**, No. 22, 47.

<sup>31</sup> B.P. 564,053; B., 1944, I, 419.

<sup>32</sup> *Trans. Electrochem. Soc.*, 1945, **87**, Preprint 30; A., 1945, I, 249.

<sup>33</sup> *J. Appl. Chem. Russ.*, 1944, **17**, 299; B., 1945, I, 337.



According to A. G. Gray,<sup>34</sup> in depositing lead from the sulphamate bath the best results are obtained by using a solution containing 150—180 g. of lead per litre, operated at a pH of about 1.5 and temperature of 24—46° using a current density of 10—120 amp. per sq. ft. When depositing on steel a primary copper strike is recommended. In a patent with E. I. Du Pont de Nemours & Co., Gray<sup>35</sup> also affirms that the covering power of lead deposited from fluoborate and sulphamate baths, especially at low current densities, is improved by the addition of anthraquinone-sulphonate thereto.

H. A. Knight<sup>36</sup> states that electrodeposited lead coatings obtained from fluoborate or sulphamate baths along with hot-dipped lead coatings are finding many outlets for protective purposes. Porosity in the deposits is not regarded as serious because the pores soon become blocked with primary products of corrosion.

*Magnesium.*—An interesting description of the Dow Company's plant at Texas for the extraction of magnesium from sea-water is given by W. P. Schambra.<sup>37</sup> He gives a detailed account of the method used for preparing the anhydrous magnesium chloride which forms the basis for the final fusion electrolysis. B. Cartwright, L. R. Michels, and S. F. Ravitz<sup>38</sup> have studied the electrolysis of magnesium into a liquid cathode using a molten magnesium chloride bath containing magnesia and carbon in suspension. Using a lead or aluminium cathode the reduced magnesium alloys therewith and may be recovered either by distillation or by electrolysis. The current efficiency approaches the theoretical value and nearly all of the chlorine evolved is available for the further conversion of magnesia into chloride. According to E. C. Houston,<sup>39</sup> it is technically possible to produce magnesium electrolytically from olivine; finely-ground olivine is extracted with hydrochloric acid to produce an impure magnesium chloride solution from which ultimately pure anhydrous chloride is prepared for electrolysis in the usual way. E. K. Lee and E. P. Pearson<sup>40</sup> have determined the electrical conductivity of mixed molten chloride melts as used in magnesium cells and in particular have examined the system magnesium chloride-calcium chloride-potassium chloride-sodium chloride containing 2% of magnesium chloride.

The standard electrode potential of magnesium has been calculated by G. E. Coates,<sup>41</sup> who, using the more precise thermal data now available and from the activity product of magnesium hydroxide, derives the new value of  $-2.375 \pm 0.005$  volts.

Most of the processes in use today for the surface protection of

<sup>34</sup> *Steel*, 1944, 115, No. 22, 78.

<sup>35</sup> B.P. 570,287; B., 1945, I, 309.

<sup>36</sup> *Met. and Alloys*, 1944, 30, 1296; B., 1945, I, 300.

<sup>37</sup> *Trans. Amer. Inst. Chem. Eng.*, 1945, 41, 35; B., 1945, I, 234.

<sup>38</sup> U.S. Bur. Mines, 1945, Rept. Invest. 3805; B., 1945, I, 269.

<sup>39</sup> *Amer. Inst. Min. Met. Eng.*, 1945, Tech. Publ. 1828; B., 1946, I, 141.

<sup>40</sup> *Trans. Electrochem. Soc.*, 1945, 88, Preprint 4; A., 1945, I, 338.

<sup>41</sup> *J.C.S.*, 1945, 480; A., 1945, I, 276.



magnesium are of the direct chemical type, but for certain purposes and with some particular alloys electrolytic treatment appears to offer advantages. The protective process devised by N. H. Simpson and P. R. Cutter<sup>42</sup> involves either a.c. or d.c. treatment in an aqueous electrolyte followed by rinsing in warm dilute chromic acid and sealing by dipping in a very dilute solution of zinc chromate primer or equivalent. Two coats of paint over the sealed deposit are said to be sufficient to ensure a high resistance to corrosion and abrasion.

*Manganese.*—In the electrodeposition of manganese from a solution containing manganese sulphate, ammonium sulphate, and sulphuric acid, C. G. Fink and M. Kolodney<sup>43</sup> recommend the use of anodes of a lead alloy containing 9—50% of tin, up to 4.4% of cobalt, and optionally up to 15% of antimony whereby formation of manganese dioxide at the anode and consequent loss of manganese is minimised. According to E. V. Potter, E. T. Hayes, and H. C. Lucans<sup>44</sup> approximately 250 c.c. of hydrogen is adsorbed in every 100 g. of electrolytic manganese. The hydrogen can be completely removed by heat-treatment in an inert gas or in hydrogen; heating in nitrogen is not recommended as up to 0.37% of that gas may be adsorbed by the metal.

*Nickel.*—The use of solutions of low pH in the deposition of nickel is discussed by E. E. Halls.<sup>45</sup> As compared with solutions of higher pH value the more acid baths, being freer from sludge formation, are cleaner in operation and permit the use of higher current densities. Owing to the increased acidity, however, the anode efficiency may exceed the cathode efficiency, and in general the flexibility is less than for solutions of the conventional type. Sulphate baths containing appreciable amounts of nickel chloride are favoured by W. L. Pinner and R. B. Kinnaman<sup>46</sup> for high-speed bright nickel plating. The optimum working conditions are a temperature of 46° and pH of 1.5; at an average current density of 100 amp. per sq. ft. it is possible to deposit 0.001 in. of nickel in 11 minutes. Organic brighteners can be incorporated in the bath while still retaining the high speed of deposition. A recent publication on current practice in the electrodeposition of nickel gives the compositions of a large number of dull and bright plating solutions.<sup>47</sup> With regard to baths of the latter type, investigation has shown that neither boric acid nor chlorides exert any influence on the brightness of the plate, but various ammonium compounds in amounts not exceeding a critical concentration for each enhance the brightness; in bright solutions of the nickel-cobalt type paraformaldehyde may be substituted for formaldehyde.

<sup>42</sup> *Iron Age*, 1944, 154, No. 14, 54.

<sup>43</sup> U.S.P. 2,320,773; B., 1945, I, 199.

<sup>44</sup> *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1809.

<sup>45</sup> *Met. Treatment*, 1944–45, 11, 235.

<sup>46</sup> *Month. Rev. Amer. Electroplaters' Soc.*, 1945, 32, 227.

<sup>47</sup> *Metal Ind.*, 1945, 66, 266, 299.



V. S. Joffe<sup>48</sup> has measured the internal tension in a number of electro-deposited metals and finds that in nickel the tensile stress increases from 13 kg. per sq. cm. to 3000 kg. per sq. cm. as the ferric ion concentration of the bath rises from 0 to 0.1N. and is also raised by the addition thereto of chromium, lead, zinc, and cadmium salts, and by aniline and other organic compounds. B. Martin<sup>49</sup> also finds that ferric ions, in addition to ferrous and aluminium ions, in electrolytes of low pH, increase the internal stress in nickel plate. Addition of potassium, sodium, magnesium, and ammonium sulphates to solutions of low pH has little effect on internal stress, but with solutions of high pH causes a marked reduction in stress. Formates, acetates, and citrates are found to decrease the stress in solutions of both high and low pH, confirming the theory that stress is caused by the co-deposition of a hydrate.

*Platinum.*—Using the oscillograph, A. Hickling<sup>50</sup> has studied the initial build-up of anodic polarisation at a smooth platinum anode and has confirmed and extended the experimental results of earlier workers; he observes three main stages in the polarisation, corresponding respectively to the ionisation of hydrogen, to the charging of a double layer, and to the deposition of oxygen at the electrode, and suggests that the last process corresponds to the formation of a unimolecular layer of platinous oxide on the surface. B. V. Erschler<sup>51</sup> has investigated the passivity of platinum and mechanism of dissolution of the metal in 15N-sulphuric acid containing various amounts of hydrochloric acid; he finds that the rate of dissolution is proportional to the surface concentration of chlorine ions and concludes that the slowest stage of dissolution is the discharge of a univalent ion.

*Silver.*—For the rapid deposition of bright silver plate, R. Weiner<sup>52</sup> recommends a cyanide bath containing selenium compounds and condensation products of albumin and fatty acids; at a current density of 2—3 amp. per sq. dm. the cathode efficiency is 100%. J. M. Sprague<sup>53</sup> has developed a method of depositing silver on chrome-molybdenum nitriding steel which ensures firm adherence even on heating to 400°. The process involves anodic etching and preliminary plating with nickel and copper; direct deposition of silver on this particular steel gives unsatisfactory results. Current American practice in the silver plating of bearings for aircraft engines is outlined by J. Geschelin.<sup>54</sup> U. A. Mullin<sup>55</sup> favours electrodeposited silver, preferably over a flash of copper or nickel, as a basis for the deposition of lead and indium in the manufacture of heavy-duty bearings.

<sup>48</sup> *Uspechi Chim.*, 1944, 13, 48; B., 1945, I, 73.

<sup>49</sup> *Proc. Amer. Electroplaters' Soc.*, June, 1944, 206.

<sup>50</sup> *Trans. Faraday Soc.*, 1945, 41, 333; A., 1945, I, 249.

<sup>51</sup> *Acta Physicochim. U.R.S.S.*, 1944, 19, 139; *J. Phys. Chem. Russ.*, 1944, 18, 131; A., 1944, I, 105.

<sup>52</sup> *Metallwirts.*, 1943, 22, 472; B., 1945, I, 302.

<sup>53</sup> *J. Electrodep. Tech. Soc.*, 1945, 20, 39; B., 1945, I, 108.

<sup>54</sup> *Automotive Ind.*, 1944, 91, No. 9, 20.

<sup>55</sup> *Month. Rev. Amer. Electroplaters' Soc.*, 1944, 31, 898.



*Tin.*—The results obtained in the American can-making industry during the war years through the substitution of electrolytically tinned steel for hot-dipped steel are discussed by J. A. Stewart and R. W. Pilcher.<sup>56</sup> R. H. Lueck and K. W. Brighton<sup>57</sup> state that enamelled electrolytic tin plate carrying 0.5 lb. of tin per basis box is quite satisfactory for can ends for packing the less corrosive foodstuffs but unenamelled cans carrying up to 0.75 lb. of tin per basis box are not suitable for packing materials of high moisture content. The authors have been unable to detect any significant difference in the corrosion-resistance of enamelled tinplate deposited from the acid and from the alkaline bath in contact with mildly corrosive packs, but when unenamelled the plate from the alkaline bath showed the better resistance to attack.

The halogen tin-plating bath introduced by E. I. Du Pont de Nemours & Co.<sup>58</sup> contains the tin as stannous chloride and an alkali or ammonium fluoride in molar concentrations bearing a definite relation to that of the stannous chloride; metals of the iron group and gelatin may also be present. This type of bath is attracting some attention in America and details of its application to the continuous plating of steel strip are given by D. A. Swalheim.<sup>59</sup> F. A. Lowenheim and F. N. Sternfels<sup>60</sup> give particulars of the potassium stannate plating bath which they initiated some few years ago and to which attention has previously been directed in these Reports.<sup>61</sup> One of the advantages of the substitution of potassium stannate for sodium stannate is the ability to use a much higher cathode current density. T. G. Timby<sup>62</sup> describes a modern strip-plating plant using this electrolyte.

From an investigation of the corrosion-resisting properties and measurements of thickness of composite coatings of electrodeposited zinc, cadmium, and nickel over electrodeposited tin on a steel base, S. Wernick<sup>63</sup> concludes that the under-coating of tin exerts a favourable influence on the distribution of the superimposed metal. He ascribes the improvement to the relatively higher hydrogen overvoltage of tin as compared with steel.

*Zinc.*—The effect of manganese on current efficiency in the electrolytic recovery of zinc has been studied by V. J. Zaidler, V. D. Ponomarev, and V. V. Stender,<sup>64</sup> who find that as the concentration of manganese in a zinc sulphate-sulphuric acid electrolyte increases the cathode potential becomes more positive. The colour of the solution indicates that permanganate is produced at the anode and its progressive reduction to manganous sulphate is held to account for the loss in current efficiency

<sup>56</sup> *Chem. Eng. News*, 1944, 22, 422; B., 1944, I, 371.

<sup>57</sup> *Ind. Eng. Chem.*, 1944, 36, 532; B., 1944, I, 371.

<sup>58</sup> B.P. 566,633; B., 1945, I, 135.

<sup>59</sup> *Iron and Steel Eng.*, 1944, 21, No. 8, 55.

<sup>60</sup> B.P. 564,489; B., 1944, I, 419.

<sup>61</sup> See *A. n. Repts.*, 1942, 27, 249; 1943, 28, 219.

<sup>62</sup> *Steel*, 1944, 115, No. 19, 124.

<sup>63</sup> *J. Electrodep. Tech. Soc.*, 1944, 20, 47; B., 1945, I, 194.

<sup>64</sup> *J. Appl. Chem. Russ.*, 1944, 17, 282; B., 1945, I, 301.



observed in the presence of manganese. W. Eckhart<sup>65</sup> has investigated the deposition of zinc from baths containing zinc sulphate, aluminium sulphate, and ammonium chloride, with and without additions of sucrose, sodium formate, and sodium sulphate. Using anodes containing small amounts of mercury and aluminium, deposition can be successfully carried out at a current density of 32 amp. per sq. dm. and pH of 3.9 to 4.1. This type of bath has poor throwing power, however, and the unavoidable presence of mercury in the plate precludes the use of the latter in contact with aluminium. Discussing the continuous zinc plating of strip steel, J. R. Erbe<sup>66</sup> states that with some modifications the process can be carried out using the type of equipment designed for continuous electro-tinning. The main difference in depositing zinc is the higher current density employed, necessitating a slower speed of throughput.

*Alloys.*—According to S. Buchan and W. D. Rae,<sup>67</sup> difficulty is frequently experienced in producing satisfactory brass electrodeposits as used in the bonding of rubber to metals. From microscopical and X-ray examination of good and bad brass deposits they conclude that non-uniformity of surface composition is responsible for poor bonding characteristics. W. Hayford and H. S. Rogers<sup>68</sup> state that with satisfactory brass deposits rubber can be bonded with a tensile strength as high as 1000 lb. per sq. in. Adhesion is dependent on depolymerisation of the rubber stock and on the formation of a copper-sulphur linkage. For the best results the brass should contain about 75% of copper.

A. H. Du Rose and P. R. Pine<sup>69</sup> describe the deposition of a nickel-iron alloy of silvery-white appearance, having a fine crystal grain size, and affording excellent resistance to corrosion and abrasion. The composition of the alloy can be closely controlled over a very wide range, the iron content of the bath rather than the current density being the determining factor. Suggested uses of the alloy are as a basis for painting and for the flash coating of other metals.

The electrodeposition of lead-tin alloys from solutions containing lead fluoborate, stannous fluoborate, fluoboric acid, boric acid, and glue is described by H. Narcus,<sup>70</sup> who has succeeded in obtaining extremely fine-grained and smooth deposits containing 35—40% of tin at a cathode efficiency approaching 100%; by altering the plating conditions alloys of other compositions can be deposited.

From a solution containing sodium stannate, sodium cuprocyanide, sodium hydroxide, and sodium cyanide, operated with copper and tin anodes on separately controlled circuits, R. M. Angles, F. V. Jones, J. W. Price, and J. W. Cuthbertson<sup>71</sup> have obtained smooth, white

<sup>65</sup> *Ind. Chem.*, 1944, 20, 524; *B.*, 1944, I, 412.

<sup>66</sup> *Iron Age*, 1944, 154, No. 20, 70.

<sup>67</sup> *Trans. Inst. Rubber Ind.*, 1945, 20, 205; *B.*, 1945, I, 301.

<sup>68</sup> *Month. Rev. Amer. Electroplaters' Soc.*, 1945, 32, 451.

<sup>69</sup> *Steel*, 1944, 114, No. 24, 124; cf. *Sheet Metal Ind.*, 1944, 20, 1739.

<sup>70</sup> *Metal Finish.*, 1945, 43, 242.

<sup>71</sup> *J. Electrodep. Tech. Soc.*, 1945-46, 21, 19; *B.*, 1946, I, 138.



deposits on steel, brass, and many other basis metals of tin-copper alloys resembling the speculum metal of the ancients. No difficulty is experienced in maintaining the composition of the alloy within close limits, and provided its tin content is within the range 39—55% the alloy can be polished to a brilliant lustre and is resistant to tarnishing in the indoor atmosphere.

*Electrolytic Polishing.*—P. Jacquet,<sup>72</sup> reviewing development in the electrolytic polishing of metals, states that, apart from its being an admirable method of finishing, the ability of the process to reveal heterogeneity and defects in the basis metal is useful in controlling rejects in production. A comprehensive survey of solutions claimed to be satisfactory for the polishing of stainless steel is given by O. Zmeskal.<sup>73</sup> One electrolyte stated elsewhere<sup>74</sup> to be satisfactory for the polishing of this material contains 55—60% of citric acid and 15—20% of sulphuric acid, and has the advantage that unwanted anode products readily precipitate, forming a sludge which is easily removed from the bottom of the vat. C. L. Faust,<sup>75</sup> on the other hand, favours a bath containing phosphoric acid and chromic acid for polishing stainless alloys; he recommends a similarly constituted bath for the polishing of nickel,<sup>76</sup> and a solution containing phosphoric acid, aluminium, and tervalent chromium for the treatment of copper.<sup>77</sup> The present status of electropolishing is reviewed by J. S. Crout<sup>78</sup>; in addition to its finishing value he states that the process is also useful for simultaneously removing small burrs and light scale.

*Miscellaneous.*—The advantages of electrodepositing metals on organic plastics are discussed by H. Narcus,<sup>79</sup> who states that plating is useful as an alternative to a wholly metallic article where the metal is in short supply and gives a product having the combined properties of the plastic and deposited metal. The most economical method of rendering the surface of the plastic conducting is to coat it chemically with silver, which for preference should be copper-plated before applying the desired electrodeposit. A. H. Stuart<sup>80</sup> favours coating with graphite and plating with copper from the sulphate bath in electrodepositing metals on non-conductors. Control of the size and orientation of the graphite flakes is important; when depositing on concrete the pores must first be sealed, either with a synthetic resin or with chlorinated paraffin.

In view of the interest at present being taken in powder metallurgy, reference should be made to the work of W. J. Kroll<sup>81</sup> on the use of fused

<sup>72</sup> *Metal Ind.*, 1945, 67, 377.

<sup>73</sup> *Metal Progr.*, 1945, 47, 729.

<sup>74</sup> *Iron Age*, 1945, 156, No. 2, 64.

<sup>75</sup> U.S.P. 2,366,712.

<sup>76</sup> U.S.P. 2,366,713.

<sup>77</sup> U.S.P. 2,366,714.

<sup>78</sup> *Metal Progr.*, 1945, 47, 259.

<sup>79</sup> *Trans. Electrochem. Soc.*, 1945, 88, Preprint 5; B., 1946, II, 18.

<sup>80</sup> *Petroleum*, 1945, 8, 25; B., 1945, I, 132.

<sup>81</sup> *Trans. Electrochem. Soc.*, 1945, 87, Preprint 5; B., 1945, I, 196.



salt electrolysis for the production of metal powders. He gives practical examples and discusses the possibilities and advantages of this type of process.

### ELECTROCHEMICAL PROCESSES.

*Electrolytic Reduction.*—The influence of structure and internal strain in various cathode metals on the electrolytic reduction of nitrobenzene to aniline has been investigated by D. N. Solanki<sup>82</sup>; he finds that the physical condition of the metal affects the current yield of aniline, which first increases slowly and then diminishes as the internal stress in the cathode increases. In the past few years a series of papers on the use of porous carbon electrodes in the electrolysis of organic solutions has been published.<sup>83</sup> N. M. Winslow<sup>84</sup> now finds that porous carbon in contact with an aqueous electrolyte and an immiscible liquid depolariser acts simultaneously as an electrode and a wick transporting the depolariser to the active face. He has examined the behaviour of these electrodes in the reduction of nitrobenzene. For reactions where carbon is not a suitable electrode material, Winslow suggests the use of porous carbon or graphite coated with metal, and claims that the combination is equivalent to a permeable metal electrode. The reduction of nitrocinnamic acids at a mercury cathode has been studied by E. P. Goodings and C. L. Wilson,<sup>85</sup> who find that in acid solution only unimolecular products are produced. In this respect the nitro-acids resemble *o*-cyano-cinnamic acid but differ from the unsubstituted chloro-, methoxy-, and hydroxy-acids, all of which on reduction yield considerable amounts of the corresponding diphenyladipic acids.

A. L. Krasilschikov and E. M. Voltschkova<sup>86</sup> find that boiler feed water can be completely deoxygenated by electrolytic reduction between iron electrodes. The oxygen is removed by cathode reduction and simultaneous absorption by ferrous hydroxide produced during the electrolysis. The cost of treatment diminishes as the temperature is raised; at a rate of flow of 3.2 litres per hr. and current density of 0.6 milliamp. per sq. cm. the power consumption is 0.3 kw.-hr. per cu. metre.

*Production of Hydrogen.*—Descriptions of open and closed unit cells, of filter-press cells, and of a modified closed unit cell developed by the Consolidated Mining and Smelting Co. for the electrolytic production of hydrogen are given by D. D. Howat.<sup>87</sup> He discusses electrolysis under high pressures and referring to the Noegerrath pressure cell states that at 200 atm. a saving of energy of 20% is possible. An investigation on the possibility of utilising electrolytic hydrogen produced under pressure as a substitute fuel has been undertaken by J. S. Just<sup>88</sup>; he employs a cell

<sup>82</sup> *Trans. Electrochem. Soc.*, 1945, 88, *Preprint* 18; B., 1946, II, 29.

<sup>83</sup> *Ibid.*, 1939, 75, 147; 1940, 77, 411; 1941, 80, 121; cf. *Ann. Repts.*, 1940, 25, 289.

<sup>84</sup> *Ibid.*, 1945, 88, *Preprint* 16; B., 1946, II, 29.

<sup>85</sup> *Ibid.*, *Preprint* 2; A., 1945, II, 359.

<sup>86</sup> *J. Appl. Chem. Russ.*, 1944, 17, 242; B., 1945, I, 313.

<sup>87</sup> *Chem. Age*, 1944, 51, 173, 197, 221; B., 1944, I, 396.

<sup>88</sup> *J. Inst. Elect. Eng.*, 1944, 91, *Part I*, 382; B., 1945, I, 21.



containing cylindrical iron gauze electrodes on either side of a tubular asbestos diaphragm.

*Production of Caustic Soda.*—H. H. Heller<sup>89</sup> ascribes the characteristic blue or purple colour of electrolytic caustic soda to the presence of a compound having the empirical formula  $C_{10}H_5O_9Cl$  which he has succeeded in isolating from a water extract of old graphite electrode ends. The compound is stated to be very stable and is not destroyed by aqua regia or by mixed nitric and sulphuric acid; it is believed to be a product of the oxidation of the graphite anodes. The idea, prevalent as recently as 1942, that the coloration is due to the iron almost invariably present in electrolytic caustic soda is thus discounted. M. J. Kermer<sup>90</sup> has developed a process for the continuous concentration of electrolytic caustic soda.

*Unclassified Processes.*—A two-stage process involving the isolation of sodium chlorate at the first stage and of potassium perchlorate at the second has been developed by J. G. Schumacher<sup>91</sup> for the continuous electrolytic production of perchlorate. The sodium chloride electrolyte is circulated through a cell equipped with graphite electrodes; sodium chlorate of 99.5% purity is formed and is removed by crystallisation, re-dissolved, further oxidised to sodium perchlorate at platinum electrodes, and by addition of potassium chloride is converted into potassium perchlorate which crystallises out. The optimum conditions for the electrodeposition from organic suspensions of plastics of the vinyl group have been worked out by F. Feinleib<sup>92</sup>; suggested applications of the process include the protection of metals from corrosion, provision of electric insulation, and the production of thin-walled plastic articles and thin plastic sheets.

### ELECTRONIC DEVICES.

The construction and applications of the magnesium-copper sulphide dry rectifier are discussed by S. Ruben.<sup>93</sup> Instead of the usual pure copper a hard, crystalline 15% zinc-copper alloy is used for the elements and on treatment in molten sulphur the surface is de-zincified and converted into a suitable form of copper sulphide. A permanent low resistance of the negative contact to the sulphide layer is ensured by the use of carbonised nickel or carbonised iron washers. Provided it is used within the stipulated limits of current density and inverse voltage this type of rectifier is stated to have a long life. According to F. Mohler,<sup>94</sup> the American steel industry, which is one of the largest consumers of direct current, now has an installed rectifier capacity of 6000 kw.

The photo-electric characteristics of silver-caesium and antimony-caesium surfaces are discussed by G. Lewin,<sup>95</sup> who appends data on

<sup>89</sup> *Trans. Electrochem. Soc.*, 1945, **87**, Preprint 9; B., 1945, I, 182.

<sup>90</sup> *Ibid.*, 1944, **86**, 157; B., 1945, I, 96.

<sup>91</sup> *Chem. Met. Eng.*, 1944, **51**, No. 12, 108; B., 1945, I, 125.

<sup>92</sup> *Trans. Electrochem. Soc.*, 1945, **88**, Preprint 6; B., 1946, II, 19.

<sup>93</sup> *Ibid.*, **87**, Preprint 21; B., 1945, I, 275.

<sup>94</sup> *Iron and Steel Eng.*, 1945, **22**, No. 10, 66.

<sup>95</sup> *Trans. Electrochem. Soc.*, 1945, **87**, Preprint 22; B., 1945, I, 274.



current output, sensitivity, dark current, and fatigue. A new method for measuring the photo-electric conductivity of zinc-cadmium sulphide phosphors involving the use of the cathode-ray oscillograph has been developed by A. E. Hardy,<sup>96</sup> who adduces evidence in support of the metastable-state theory of the mechanism of luminescence. H. D. Rentschner and D. E. Henry<sup>97</sup> find that the photo-electric work functions of zirconium, titanium, thorium, and similar metals are moved towards the longer wave-lengths when the metals react with oxygen and ascribe the shift to the formation of a solid solution of the gas in the metal. In the selenium photo-cell devised by E. Körber<sup>98</sup> a thin layer of cadmium oxide is superimposed on the selenium and is then reduced at the surface to metallic cadmium by subjection to a glow discharge in hydrogen.

Present-day applications of electronic devices in industry are discussed by R. Roberson.<sup>99</sup> As regards photo-cells an interesting application, due to N. Ahmad and R. L. N. Iyenagar,<sup>100</sup> is the measurement of the average diameter of fine wires and filaments. E. Glückauf<sup>101</sup> describes a photo-electric method for measuring directly the ratio of two illuminations, whilst A. J. Brunner<sup>102</sup> gives particulars of a photo-electric exposure meter designed specifically for metallographic purposes, claimed to give accurate exposure times for all types of microstructure. Further uses of electronic devices in metallurgical research, including their application to the measurement of temperature, damping capacity, and magnetic hysteresis, are mentioned by E. V. Potter.<sup>103</sup> An electronic flow meter for measuring and automatically recording small rates of flow or the average rate under pulsating flow, covering a velocity range of 1—200 ml. per minute, has been perfected by E. C. Crittenden, jun., and R. E. Shipley.<sup>104</sup>

### INSULATION MATERIALS.

T. A. Klinefelter, S. Speil, and S. Gottlieb<sup>105</sup> have examined the suitability of American talcs for the manufacture of high-frequency insulators. Satisfactory material is obtainable from Nevada, Montana, and elsewhere, but the large deposits available in New York and Alabama are too abrasive or too high in iron although in the authors' opinion they could be made serviceable by beneficiation.

W. G. Thomson<sup>106</sup> finds that the contamination of porcelain insulators by airborne particles is attributable in part to aërodynamic conditions. E. M. Cohn and P. G. Guest<sup>107</sup> provide data on the influence of humidity

<sup>96</sup> *Trans. Electrochem. Soc.*, 1945, **87**, *Preprint* 27; A., 1945, I, 262.

<sup>97</sup> *Ibid.*, *Preprint* 14; A., 1945, I, 285.

<sup>98</sup> U.S.P. 2,317,776; B., 1945, I, 208.

<sup>99</sup> *Iron and Steel Eng.*, 1945, **22**, No. 10, 59.

<sup>100</sup> *Current Sci.*, 1944, **13**, 256; C., 1945, 140.

<sup>101</sup> *J. Sci. Instr.*, 1945, **22**, 34; C., 1945, 141.

<sup>102</sup> *Met. and Alloys*, 1945, **22**, 416.

<sup>103</sup> U.S. Bur. Mines, 1944, *Tech. Paper* 661; C., 1945, 78.

<sup>104</sup> *Rev. Sci. Instr.*, 1944, **15**, 343; C., 1945, 145.

<sup>105</sup> U.S. Bur. Mines, 1945, *Rept. Invest.* 3804; B., 1945, I, 258.

<sup>106</sup> *J. Inst. Elect. Eng.*, 1944, **91**, Part II, 317; B., 1944, I, 348.

<sup>107</sup> U.S. Bur. Mines, 1944, *Inf. Circ.* 7286; B., 1945, I, 243.



on the resistivity of solid dielectrics and dissipation of static electricity. Referring to the dielectric heating of cellulose and cellulose-filled phenolic laminating materials, T. W. Dakin and R. W. Auxier<sup>108</sup> state that heat is generated in the materials by ionic oscillation and dipole rotation, both of which phenomena vary with frequency.

As a means of differentiating between the two main types of degradation products occurring in oil-paper dielectrics, J. D. Piper and N. A. Kerstein<sup>109</sup> have investigated the use of a.c. electrical conductivity measurements. J. A. van den Akker<sup>110</sup> uses a shielded conjugate Schering bridge in conjunction with a source of a.c. of variable frequency for determining the dielectric constant and power factor of paper dielectrics; before testing the samples are thoroughly dried and the test condenser is placed in a chamber at a pressure of  $10^{-6}$  atm. and, if necessary, is heated.

The effect of spraying in an electrostatic field on the uniformity of deposition of porcelain enamels and on the amount of waste or overspray has been studied by J. B. Willis.<sup>111</sup> The process leads to an improvement in uniformity of deposition and reduction in overspray which, it is contended, would amount to 15–20% on an industrial scale, and is applicable to the automatic spraying of flat surfaces and symmetrical shapes.

### SECONDARY CELLS.

The effect of plate formation temperature on the initial cold capacity of lead accumulators has been investigated by T. C. Lynes, F. Hovorka, and L. E. Wells,<sup>112</sup> who find that the temperature at which unformed or discharged active paste material is transformed into charged active material exerts a critical influence on the capacity. Greatly improved cold capacity accompanied by only a minor decrease in life is attainable by keeping the plates cool during formation, especially in the first half of the forming cycle. H. Haebler<sup>113</sup> favours coating the positive or negative grids of lead cells with tin as a means of increasing the storage capacity of the paste. The coating of antimonial-lead accumulator grids with pure lead, either by electrodeposition or by an alternative method, is recommended by E. W. Smith<sup>114</sup> as a means of preventing the formation of a local couple with the antimony liberated from the positive grid and eventually deposited on the negative grid, and also of suppressing the dissolution of antimony from the positive grid. According to K. Hofer<sup>115</sup> the efficiency of nickel-iron accumulators of the Edison type can be increased by adding lithium hydroxide to the electrolyte. Provided the active mass of the cathode is increased by 40% it is in this way possible to increase the capacity of the cell by as much as 40% without increasing the mass of the active nickel anode.

<sup>108</sup> *Ind. Eng. Chem.*, 1945, **37**, 268; B., 1945, I, 169.

<sup>109</sup> *Ibid.*, 1944, **36**, 1104; C., 1945, 145.

<sup>110</sup> *Paper Trade J.*, 1944, **119**, *TAPPI Sect.*, 253; C., 1945, 145.

<sup>111</sup> *J. Amer. Ceram. Soc.*, 1945, **28**, 121; B., 1945, I, 294.

<sup>112</sup> *Ind. Eng. Chem.*, 1945, **37**, 776; B., 1946, I, 46.

<sup>113</sup> U.S.P. 2,317,759; B., 1945, I, 117.

<sup>114</sup> U.S.P. 2,193,782—3; B., 1945, I, 247.

<sup>115</sup> *Batterien*, 1944, **12**, 257.



# FATS, FATTY OILS, AND DETERGENTS.

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INCREASED activity is again evident in research on subjects which relate to the fat and detergent industries. In the selected topics mentioned in this Report, the following may have special interest: work on combination of fats with oxygen (both in regard to edible fat rancidity and to drying oils), the antioxidant question, procedures for determining the detailed composition of the more unsaturated oils, studies of linseed oil composition, the component acids of various animal milk fats, and some proposed new methods for glycerin recovery.

## DETERGENTS.

Work in this section concerns a variety of somewhat disconnected topics, not easily woven into a connected story.

*The Saponification Process.*—W. Gallay and I. E. Puddington<sup>1</sup> have shown that fats and commercial "acid oils" are completely and rapidly saponified at about 60° when mixed with a suspension in mineral oil of finely dispersed sodium or calcium hydroxide. H. G. Kirschenbauer,<sup>2</sup> dealing with soap boils on a laboratory scale, has recommended (in preference to settling by gravity) that the finished soap should be centrifuged at a temperature above its melting point for a short time and then allowed to solidify in the centrifuge cups, in order to effect rapid and reproducible separation of the nigre from the neat soap. The recently discovered<sup>3</sup> "kettle-wax" phase of soap which may be formed during boiling has been confirmed by studies on sodium stearate and sodium laurate, in equilibrium with sodium chloride and water, due to J. W. McBain and co-workers<sup>4</sup>; from data obtained by various methods (analytical, visual, and microscopical), phase-rule diagrams have been constructed which define the equilibrium boundaries of the "kettle-wax" phase.

*Physical Constitution of Soaps and Soap Solutions.*—Two further X-ray diffraction studies of soaps may be mentioned. R. H. Ferguson and H. Nordsieck<sup>5</sup> have investigated binary mixtures of anhydrous soaps such as sodium laurate-palmitate etc., and also some commercial soaps; examination of the long X-ray spacings shows that separation of individual constituents in the solid phase does not occur, the separated

<sup>1</sup> *Canad. J. Res.*, 1944, 22, B, 76; A., 1944, I, 201.

<sup>2</sup> *Oil and Soap*, 1944, 21, 237; C., 1945, 28.

<sup>3</sup> *Ann. Repts.*, 1943, 28, 229.

<sup>4</sup> *Ind. Eng. Chem.*, 1944, 36, 808; *Oil and Soap*, 1944, 21, 227; B., 1945, II, 244, 24; C., 1945, 28.

<sup>5</sup> *Ind. Eng. Chem.*, 1944, 36, 748; B., 1945, II, 245.



solids being one or more solid solution phases. E. W. Hughes, W. M. Sawyer, and J. R. Vinograd<sup>6</sup> have shown that an isotropic solution of potassium laurate contains ordered aggregates of micelles which give X-ray diffraction patterns.

R. D. Vold and M. J. Vold<sup>7</sup> have shown the existence of from three to five transition temperatures in palmitates of the alkali metals, as the result of colorimetric, dilatometric, and microscopical examinations.

*Surface Activity, Detergency, etc. of Soaps and of Synthetic Detergents.*—The Liversidge lecture on "Reactions in Monolayers" by E. K. Rideal,<sup>8</sup> although not directly concerned with detergent action, will be of value to those interested in surface activity, especially the description of experiments on the rate of hydrolysis by aqueous sodium hydroxide of monolayers of esters of long-chain alcohols or acids.

R. C. Merrill and F. T. Moffett<sup>9</sup> have described standardised apparatus and procedures for determining the foam stability of detergent solutions by either the "foam drainage" or the "foam time" (life of the foam monolayer) methods. The influence of pH, temperature, concentration of solution, presence of calcium or magnesium ions, and other factors on the foam stability of solutions of soaps of some individual fatty acids has been studied by G. D. Miles and J. Ross.<sup>10</sup> The inhibition, when certain other compounds are present, of foam produced by good foam-producing detergents has been examined by S. Ross and J. W. McBain<sup>11</sup> in regard to twenty-two organic compounds of differing constitution and known to behave as foam-destroying agents; long-chain alkyl phosphates are specially effective in this respect, but no general explanation of the mechanism by which such compounds destroy foam has yet emerged.

J. L. Wilson and E. E. Mendenhall<sup>12</sup> have given details of a standardised photometric method whereby the thickness of films deposited on transparent glass by the interaction of detergents and hard water can be measured; the relative value of added inorganic sodium salts in retarding precipitation of lime soaps was observed to be, in decreasing order, pyrophosphate, phosphate, metasilicate, carbonate. J. C. Harris and E. L. Brown<sup>13</sup> have reported that very dilute (0.05—0.2%) solutions of sodium laurylsulphonate have little detergent power in hard water, unless fortified by the alkaline inorganic salts just mentioned, which they also place in the same order of relative effectiveness as Wilson and Mendenhall.

The detergent properties of solutions of sodium salts of a very large

<sup>6</sup> *J. Chem. Physics*, 1945, 13, 131; A., 1945, I, 198.

<sup>7</sup> *J. Physical Chem.*, 1945, 49, 32; A., 1945, I, 137.

<sup>8</sup> *J.C.S.*, 1945, 423; A., 1945, I, 277.

<sup>9</sup> *Oil and Soap*, 1944, 21, 170; C., 1945, 28.

<sup>10</sup> *J. Physical Chem.*, 1944, 48, 280; A., 1945, I, 59.

<sup>11</sup> *Ind. Eng. Chem.*, 1944, 36, 570; B., 1944, II, 301.

<sup>12</sup> *Ibid. [Anal.]*, 1944, 16, 251, 253; C., 1944, 198.

<sup>13</sup> *Oil and Soap*, 1945, 22, 3; B., 1945, II, 221.



number of *n*- and *sec.*-alkyl (long-chain,  $C_{11}$  to  $C_{19}$ ) sulphates have been studied in considerable detail by R. G. Aickin<sup>14</sup> and by G. D. Miles, J. Ross, and co-workers.<sup>15</sup> The preparation of further new types of detergents in which the long-chain group is part of the complex cation ("invert soaps"<sup>16</sup>) has been given by P. Rumpf and R. Kwass<sup>17</sup> (di- and mono-alkylaminoethanols, *e.g.*, didodecylaminoethanol, di- and mono-benzylaminoethanol) and by W. F. Hart and J. B. Niederl<sup>18</sup> (long-chain alkyl quaternary thiomorpholinium salts).

The Soap Analysis Committee<sup>19</sup> of the A.O.C.S. has issued full details of their present standard methods for the analysis of ordinary soaps and of special soaps containing synthetic detergents.

#### GLYCERIN.

The possibility, when producing crude glycerin, of avoiding the evaporation of water from dilute aqueous glycerin solutions (soap lyes or fermentation liquors) is brought to notice again by two processes claimed in patents which have been published recently. N. M. Mnookin<sup>20</sup> has proposed the solvent extraction of glycerin from dilute aqueous solutions by a suitable mixture of a compound miscible with water with another compound immiscible with water but miscible with the first compound (a mixture of 1 part of isopropyl and 2 parts of *n*-butyl alcohol is suggested). After agitation and settling, the glycerin is recovered from the solvent layer by evaporation of the latter. The Colgate-Palmolive-Peet Co.<sup>21</sup> has put forward a project whereby (after prior removal of free fatty acid, if necessary, by a selective solvent, *e.g.*, alcohol) the fatty glycerides are treated with an alcohol in presence of a catalyst such as sodium hydroxide, so that a mixture of fatty alkyl esters and glycerin (with excess of alcohol) is produced; the mixture is separated by distillation, first at atmospheric pressure and then in a vacuum.

#### EDIBLE FATS: RANCIDITY.

##### *Component Acids of Milk Fats.*

Several detailed accounts of the components of various milk fats have appeared since the last Report, and may conveniently be mentioned at this point. A. R. Baldwin and H. E. Longenecker<sup>22</sup> have given data for the component acids of cow colostrum fat; the results show little difference from those for typical cow milk fats, although the saturated acids of lower molecular weight than palmitic appear on the whole to

<sup>14</sup> *J. Soc. Dyers and Col.*, 1944, 60, 170; B., 1944, II, 360.

<sup>15</sup> *Ind. Eng. Chem.*, 1944, 36, 610; A., 1945, II, 74.

<sup>16</sup> Cf. *Ann. Repts.*, 1944, 29, 238.

<sup>17</sup> *Bull. Soc. chim.*, 1943, [v], 10, 347; A., 1945, II, 309.

<sup>18</sup> *J. Amer. Chem. Soc.*, 1944, 66, 1610; A., 1945, II, 70.

<sup>19</sup> *Oil and Soap*, 1945, 22, 62; C., 1945, 173.

<sup>20</sup> U.S.P. 2,194,665; B., 1945, II, 293.

<sup>21</sup> U.S.P. 2,383,579, 2,383,580, 2,383,581, 2,383,596, 2,383,599, 2,383,601, 2,383,602, 2,383,614, 2,383,632, 2,383,633.

<sup>22</sup> *J. Biol. Chem.*, 1944, 155, 407; A., 1945, III, 103.



be in slightly lower proportions, and the palmitic acid in somewhat higher proportion, in the colostrum than in the full milk fats.

The component acids of the milk fats of the goat, ewe, and mare have been determined by T. P. Hilditch and H. Jasperson.<sup>23</sup> The figures for goat and ewe milk fats confirm the results of previous work, especially the presence of more decoic acid than is present in cow milk fat; mare milk fat, not hitherto studied in detail, had a content of less than 1% (wt.) of butyric and hexoic acid, and low (15%) palmitic acid, whilst the unsaturated acids included, as well as oleic (16%) and octadecadienoic (7%), hexadecenoic (7%) and 14% of linolenic acid (not present in most other milk fats, but characteristic for horse depot fats). Spectrographic examination (after alkali isomerisation) by the same workers<sup>24</sup> of unsaturated  $C_{18}$  acid fractions from cow and goat milk fats and from grass fats has confirmed the presence in the milk fats of forms of octadecadienoic acids other than ordinary linoleic acid, whilst the grass fat was shown to contain large proportions of triene  $C_{18}$  acids isomeric, but not identical, with linolenic acid.

The component glycerides of human milk fat were submitted to fractional crystallisation, followed by detailed examination of the four resulting fractions, by T. P. Hilditch and M. L. Meara,<sup>25</sup> who found that the chief components were glycerides with two unsaturated groups and one saturated group ( $C_{10}$ ,  $C_{12}$ , or  $C_{14}$ ) 24, mono-unsaturated mono- ( $C_{10}$ ,  $C_{12}$ , or  $C_{14}$ )-palmitin 20, palmitodiunsaturated 19, mono-unsaturated palmitostearin 14, and fully-saturated, mainly mono- ( $C_{10}$ ,  $C_{12}$ , or  $C_{14}$ )-palmitostearin 9% (mol.). Oleic acid is probably almost the sole unsaturated component of the mono-unsaturated glycerides, and a further 9% of the glycerides are probably dioleoglycerides in which the third acyl group is one of the minor component unsaturated acids (linoleic, hexadecenoic, etc.).

#### *Comparative Nutritive Values of Butter and Other Fats.*

Further reports on this subject are almost unanimously in favour of the view that edible vegetable fats are at least equal to butter in promoting the growth of rats. H. J. Deuel and co-workers<sup>26</sup> have observed that when lactose is the sole source of carbohydrate rats develop alopecia and ultimately die, whatever the dietary fat; that the growth of young rats (over 200), fed for twelve weeks from weaning on controlled diets in which the fat was a vitaminised vegetable oil (or margarine), was identical with that of similar diet in which the fat was butter; and that either fat diet gave the same results with ten successive generations, so that the fats in margarine serve adequately in place of butter both for growth and reproduction, providing that the diet is otherwise nutritionally satisfactory. R. K. Boutwell, R. P. Geyer, C. A. Elvehjem,

<sup>23</sup> *Biochem. J.*, 1944, 38, 443; *A.*, 1945, III, 182.

<sup>24</sup> *J.S.C.I.*, 1945, 64, 109; *A.*, 1945, III, 456.

<sup>25</sup> *Biochem. J.*, 1944, 38, 437; *A.*, 1945, III, 181.

<sup>26</sup> *J. Nutrition*, 1944, 28, 225; 1945, 29, 237, 309; *A.*, 1945, III, 114, 550.



and E. B. Hart,<sup>27</sup> whose reports in 1940 that the more saturated butter fat was superior to vegetable oils in nutritive value gave rise to most of the recent voluminous output on this topic, have now admitted that growth rates are equal on butter fat or on maize oil diets if the carbohydrate in the food is glucose or a glucose-galactose mixture whatever the vitamin level; and that the inferiority of maize oil with lactose, sucrose, dextrin, etc. rations can be improved or eliminated by raising the level of the vitamin-B complex and adding high levels of certain other advitants. Agreement would appear to be reached, therefore, that *cæteris paribus* the soft vegetable oils are in no way inferior to butter in nutritive value.

E. F. Brown and W. R. Bloor<sup>28</sup> separated butter fatty acids into five fractions (volatile, low-molecular liquid, high-molecular liquid, low-molecular solid, and high-molecular solid), and substituted each fraction for butter fat in a normal rat diet; the liquid acids were well absorbed, led to increase in body weight equal to or better than those with butter, and promoted utilisation of carotene better than the solid acids, whilst the latter and also the volatile acids were less well absorbed and gave inferior growth results compared with butter fat or the liquid acids. K. F. Mattil and J. W. Higgins<sup>29</sup> administered mixed tristearin and triolein, or oleodistearin, to rats, and found that, although stearic acid was poorly utilised in any case, the mixed glycerides were better utilised than mixtures of tristearin and triolein; possible selective utilisation of fatty acids is suggested, and it is considered that either hydrolysis of the glycerides or ester-interchange may precede assimilation.

#### *Studies on Fat Metabolism.*

*Fat Absorption.*—A. C. Frazer and his colleagues<sup>30</sup> have produced evidence in further support of his contention that absorption of ingested fat from the small intestine does not involve hydrolysis and resynthesis of the fat. They have shown that such absorption involves a particle size of less than  $0.5\ \mu$ . diameter in an emulsion which must be spontaneous, and stable for 3 hours between pH 6.0 and 8.5. Study of emulsions from ternary mixtures of fatty acid, monoglycerides, soap, cholesterol, and bile salts has shown that only the system monoglyceride-fatty acid-bile salts fulfils all the conditions. Bile salts are known to be present in suitable amounts, whilst, in the paper finally quoted, it has been shown that, in the first five hours of pancreatic lipolysis of olive oil, no free glycerol is produced but the acetyl value rises to about 64 (equivalent to about 20% or so of monoglyceride). Moreover, monoglycerides were recovered from the intestines of rats and identified after

<sup>27</sup> *Arch. Biochem.*, 1945, 7, 143; A., 1945, III, 773.

<sup>28</sup> *J. Nutrition*, 1945, 29, 349; A., 1945, III, 550.

<sup>29</sup> *Ibid.*, 255; A., 1945, III, 550.

<sup>30</sup> *J. Physiol.*, 1944, 103, 5P, 6P, 306; *Biochem. J.*, 1945, 39, 122; A., 1945, III, 32, 447, 638.



separation by condensation with phthalic anhydride. The evidence in favour of the above emulsification system (requisite for transmission of fat glycerides) being normally present in the small intestine thus appears to be well established.

*Fatty Acid Mobilisation.*—An important contribution to the operation of “ $\beta$ -oxidation” *in vivo* during the catabolism of fatty acids has been made by S. Weinhouse, G. Medes, and N. F. Floyd,<sup>31</sup> who have incubated with sliced rat liver *n*-octoic, *n*-butyric, and acetic acid, in the carboxyl groups of which some proportion of the carbon was the heavy isotope  $^{13}\text{C}$ . The original  $\beta$ -oxidation hypothesis presupposed that fission of a  $\text{C}_4$  chain (terminating in a carboxyl group and leading to acetoacetic acid and acetone) took place, whilst the later view of “multiple alternate oxidation” suggested that successive  $\text{C}_4$  fragments might be simultaneously produced throughout the chain of carbon atoms in a higher fatty acid. Examination of the distribution of  $^{13}\text{C}$  in the acetoacetic acid, acetone, and carbon dioxide produced during the authors’ experiments has, however, established fairly clearly that scission into  $\text{C}_2$  units first takes place (“ $\beta$ -oxidation”), but that this is followed by condensation of two of these units in order to produce acetoacetic acid and acetone. The authors say that their results indicate that the final reaction proceeds by coupling of two acetyl groups, but that the possibility of the metabolism of acetate by some other pathway not involving ketone formation is not excluded.

#### *Animal Body Fats (Edible).*

*Pig Body Fats.*—F. B. Shorland and P. B. D. de la Mare,<sup>32</sup> in studies of bacon pig fats in relation to carcase quality, have shown that, when copra is included in the diet, the fat may contain up to 13% of myristic and 4% of lauric acids, and that these acids are more readily laid down by fast-growing pigs, whereas linoleic acid is more richly deposited in animals of slow growth. The “growth rate” theory of E. H. Callow<sup>33</sup> explains variation in iodine value in pig depot fats at various rates of growth, but does not cover the actual fatty acid composition. The differing composition of fats from different depots of the same animal is probably characteristic for depot and species and is not, in the authors’ view, readily altered by dietary change. The same authors<sup>34</sup> have also made a careful study of the unsaturated  $\text{C}_{20}$  acids from 4 kg. of pig back fat, and find that eicosenoic acid amounts to 0.5% of the total acids; eicosa-di- and -tri-enoic acids, and also arachidonic acid, are present, but only in very small amounts, and no evidence of unsaturated  $\text{C}_{22}$  acids was observed.

<sup>31</sup> *J. Biol. Chem.*, 1944, **153**, 689; **155**, 143; 1945, **157**, 35; **158**, 411; *A.*, 1944, **III**, 676; 1945, **III**, 185, 382, 556.

<sup>32</sup> *J. Agric. Sci.*, 1945, **35**, 33, 39; *A.*, 1945, **III**, 302.

<sup>33</sup> *Empire J. Exp. Agric.*, 1935, **3**, 80; *B.*, 1935, 781.

<sup>34</sup> *Analyst*, 1944, **69**, 337; *Nature*, 1945, **155**, 48; *Biochem. J.*, 1945, **39**, 246; *A.*, 1945, **III**, 34, 865.



*Glyceride Structure of Lards and Tallows.*—R. W. Riemenschneider, F. E. Luddy, M. L. Swain, and W. C. Ault<sup>35</sup> have separated lards and tallows into seven fractions by systematic crystallisation from acetone between 20° and -45°, and determined the composition of each fraction from spectrographic analysis (cf. below) and iodine values. From the component acids of the fractions they have deduced the component glycerides in each case, noting that the tallows contain much more trisaturated and disaturated glycerides than the lards which, conversely, are richer in monosaturated and in triunsaturated glycerides; the triunsaturated glyceride content of lard is stated to be definitely greater than hitherto suggested by previous work.

*Hydrogenated Linseed Oil (Edible).*

H. W. Lemon<sup>36</sup> has examined the acids present in linseed oil which had been hydrogenated to an iodine value of 82; the octadecadienoic acids were separated by low-temperature crystallisation as a concentrate containing 68%, but spectrographic tests showed the presence of only about 7% of linoleic acid. Lemon hence concluded that the  $\Delta^{12}$ -ethenoid bond in linolenic glycerides is preferentially hydrogenated, furnishing  $\Delta^{9:15}$ -octadecadienoic acid (incapable of isomerisation by alkali to a conjugated diene acid). Further, he suggested that the marked "reversion" odour and flavour of hydrogenated linseed oil may be ascribed to this isolinoleic acid or to a decomposition product thereof. J. G. Armstrong and W. D. McFarlane,<sup>37</sup> studying the use of hydrogenated linseed oils in cooking fats (pastry shortenings), have confirmed Lemon's view that some specific compound formed during the hydrogenation is responsible for the specially-marked "reversion" flavour in the baked products; they have shown that the degree of flavour reversion runs parallel with developing peroxide value, although its onset precedes the end of the induction period, and that antioxidants reduce but do not eliminate the reversion. Since they also show that the trouble does not occur with sunflower seed oil or hydrogenated sunflower seed oil, nor with these oils when mixed either with unsaponifiable matter from linseed oil or with ethyl linolenate, Lemon's conclusion that a specific partial hydrogenation product of linolenic glycerides is responsible (probably owing to special proneness to oxidation or development of specific oxidation products) receives considerable support from these observations.

*Rancidity.*

*Oxidative Tests.*—The ferric thiocyanate method<sup>38</sup> of determining active oxygen in oxidised fats gives higher values than those determined iodometrically, and C. H. Lea<sup>39</sup> has shown that this is due to sensitivity

<sup>35</sup> A.O.C.S., 19th Autumn Meeting, Chicago, Proc., 1945.

<sup>36</sup> *Canad. J. Res.*, 1944, 22, F, 191, 295; B., 1945, II, 83; 1946, II, 15.

<sup>37</sup> *Oil and Soap*, 1944, 21, 322; B., 1945, III, 76.

<sup>38</sup> *Ann. Repts.*, 1944, 29, 240.

<sup>39</sup> *J.S.C.I.*, 1945, 64, 106; C., 1945, 181.



of the reagent to oxygen, recommending that oxygen should be rigorously excluded from the medium during the measurement of peroxide values. In a more general survey of the determination of peroxide values of fats, C. B. Stuffins and H. Weatherall<sup>40</sup> have also concluded that further oxidation is effectively minimised only when inert gas is used for passage through the reaction mixture, and they prefer to carry out the determinations at room temperature. J. J. Nagy, B. W. Beadle, and H. R. Kraybill<sup>41</sup> have suggested that the use of dry oxygen or air is preferable in stability tests by either the active oxygen or the oxygen absorption (Barcroft-Warburg) methods; although in some cases little difference in results is shown, in others (especially in presence of certain antioxidants) the oxidation is much retarded when moist air is used. Comparative studies of the keeping qualities of lards, alone or with a variety of antioxidants, as indicated by peroxide development, absorption of oxygen at 100° (Barcroft-Warburg), or storage at room temperature with flavour tests, have been made by J. J. Nagy, F. C. Vibrans, and H. R. Kraybill<sup>42</sup> and by R. W. Riemenschneider and co-workers.<sup>43</sup> Both groups of workers agree that the keeping qualities indicated by the different methods do not always accord, especially when certain antioxidants are being used, although in many instances there is general agreement or parallelism. Nagy *et al.* stress the need for caution in the interpretation of accelerated oxidation tests (cf. also p. 280) and for correlation of the latter with tests made under normal conditions of storage.

*Antioxidants.*—In a paper entitled “Antioxidants and Synergists,” H. A. Mattill<sup>44</sup> has contributed a most useful review of the general state of knowledge of this field. *Antioxidants* are actual inhibitors of autoxidation in fats, characterised in nearly all instances by presence in their molecules of one or more *o*- or *p*-di- or poly-phenolic groups; *synergists* have little if any antioxidant power but reinforce the action of many antioxidants. The latter group includes hydroxy-acids, dicarboxylic acids, phosphoric acid, etc., and Mattill also places ascorbic acid and its analogues in this category, although more usually it is considered as a true antioxidant. According to Mattill, kephalin (but not lecithin) is also a synergist.

Concerning methods of evaluation of efficacy of added antioxidants, E. L. Hove and Z. Hove<sup>45</sup> have proposed to measure the rate of destruction (by the autoxidised fat peroxides) of added carotene as a measure of antioxidant efficiency, but point out that, over the critical initial period, there is lack of correlation between carotene destruction tests at 35° and development of peroxide values in aëration tests at 95°. A. J.

<sup>40</sup> *Analyst*, 1945, **70**, 403; C., 1946, 22.

<sup>41</sup> *Oil and Soap*, 1945, **22**, 123; C., 1945, 171.

<sup>42</sup> *Ibid.*, 1944, **21**, 349; B., 1945, **II**, 181; C., 1945, 181.

<sup>43</sup> *Ibid.*, 1945, **22**, 23, 174; B., 1945, **II**, 344, 345.

<sup>44</sup> *Ibid.*, 1; B., 1945, **II**, 219.

<sup>45</sup> *J. Biol. Chem.*, 1944, **156**, 611; A., 1945, **III**, 377; C., 1945, 118.



Stirton, J. Turer, and R. W. Riemenschneider<sup>46</sup> measured the oxygen uptake at 100° of methyl oleate, linoleate, and linolenate and of lard esters with and without a number of antioxidants, finding an additive relationship for the component unsaturated acids in the lard esters, and finding the same order of efficacy for the antioxidants in both the lard esters and the original lard. Further reference to these results will be made when discussing autoxidation from a more general point of view (p. 280). The fate of added antioxidant during its protective action on fats has been studied by D. F. Filer, K. F. Mattil, and H. E. Longenecker<sup>47</sup> in the cases of gallic acid and of ascorbic acid. Whilst the former disappears wholly before the end of the induction period, ascorbic acid disappears at first rapidly and then more slowly but never completely, an appreciable amount remaining after the sharp rise in peroxide value eventually sets in.

Comparative efficiencies of the more prominent antioxidants at present under notice in regard to stabilising refined lard, vegetable oils, and baked goods (biscuits) have been recorded by J. W. Higgins and H. C. Black,<sup>48</sup> whilst similar data for antioxidants used to protect carotene added to cacao butter, coconut fat, refined cottonseed oil, and lard have been given by E. Bickoff, K. T. Williams, and M. Sparks,<sup>49</sup> who mention that carotene was found to be extremely stable in cacao butter.

Steam-deodorisation is stated by A. E. Bailey and R. O. Feuge<sup>50</sup> to improve the stability of slightly oxidised fats, the improvement being greater if traces of commercial lecithin or of phosphoric acid are added to the deodorised fat, whilst a still greater effect was attained by adding either of the compounds named to the fat prior to steam-deodorisation. Somewhat similarly, R. W. Riemenschneider, S. F. Herb, E. M. Hammaker, and F. E. Luddy<sup>51</sup> have observed that steam-deodorisation has little effect on the keeping power of steam-rendered lard but substantially increases that of kettle-rendered lard; these workers examined the concurrent influence of addition of compounds such as tocopherol or nordihydroguaiaretic acid, finding that, with this type of antioxidant, addition was more effective after than prior to deodorisation.

Tocopherol concentrates suitable for use as fat-antioxidants may be produced, as shown by W. S. Singleton and A. E. Bailey,<sup>52</sup> either by molecular distillation from groundnut oil or by fractional crystallisation (from acetone at -60° to -70°) of hydrogenated cottonseed oils, when 95% of the tocopherol in the original oil may be obtained as a 30% concentrate after evaporation of the acetone from the most soluble fraction.

<sup>46</sup> *Oil and Soap*, 1945, 22, 81; A., 1945, I, 278.

<sup>47</sup> *Ibid.*, 1944, 21, 289; B., 1945, II, 113; C., 1945, 118.

<sup>48</sup> *Ibid.*, 277; B., 1945, II, 142.

<sup>49</sup> *Ibid.*, 1945, 22, 128; B., 1945, II, 273.

<sup>50</sup> *Ibid.*, 1944, 21, 286; B., 1945, II, 113.

<sup>51</sup> *Ibid.*, 307; B., 1945, II, 114.

<sup>52</sup> *Ibid.*, 188, 224; B., 1944, II, 359; 1945, II, 23.



C. E. Swift, G. E. Mann, and G. S. Fisher<sup>53</sup> have given evidence in support of the view that the reddish colour of autoxidised cottonseed oil is due to the oxidation of  $\gamma$ -tocopherol to a chroman-5 : 6-quinone.

#### DRYING OILS : AUTOXIDATION.

*Autoxidation.*—In continuation of the work of E. H. Farmer and his collaborators,<sup>54</sup> J. L. Bolland and H. P. Koch<sup>55</sup> have studied the autoxidation of ethyl linoleate in oxygen in the dark at 45°. The primary product is a monohydroperoxide, shown spectrographically to contain a large proportion of conjugated diene isomerides resulting from rearrangement of the system  $\cdot\text{C}:\text{C}\cdot\text{C}\cdot\text{C}:\text{C}\cdot$ . Similar evidence suggests that one of the early secondary products arising from further change of the peroxide is ketonic in character. The results obtained harmonised fully with Farmer's postulated free-radical mechanism of the autoxidation reaction.

F. D. Gunstone and T. P. Hilditch<sup>56</sup> have discussed the changes in peroxide value, iodine value, and production of conjugated systems which proceed during the prolonged autoxidation in diffused daylight in oxygen of methyl oleate, linoleate, and linolenate at 20° and at higher temperatures. With methyl oleate the process was very slow at 20°, somewhat faster at 50°, but very rapid from 80° upwards, so that at the higher temperature oxidation apparently may differ essentially in character from that at room temperature. With methyl linoleate the temperature coefficient appeared more constant over the range 20° to 80°. Development of conjugated diene unsaturation to a maximum, followed by a decline, was roughly parallel with the formation and subsequent partial disappearance of peroxides in all autoxidations of methyl linoleate or linolenate. The relative rates of autoxidation of methyl oleate, linoleate, and linolenate at 20° were 1 : 12 : ca. 25, the presence of the system  $\cdot\text{C}:\text{C}\cdot\text{C}\cdot\text{C}:\text{C}\cdot$  causing a marked increase in ease of union with oxygen, the central  $-\text{CH}_2-$  group probably being rendered more active by the two adjacent polar ethenoid groups. The change in temperature coefficient above 80° (up to 120°) caused these authors to throw further doubt on the value of accelerated oxidation tests conducted at 100° or even higher in assessing stability of edible fats to oxidation. On the other hand, the results of Stirton, Türrer, and Riemenschneider<sup>46</sup> (p. 279) lead to relative rates of oxidation at 100° (Barcroft-Warburg method) for methyl oleate, linoleate, and linolenate of about 1 : 10 : 16, *i.e.*, not widely different from the data of Gunstone and Hilditch at 20°. Moreover, Riemenschneider *et al.* state that from their data it is possible to predict additively the oxidation rates for mixtures or for lard esters (in the latter instance, however, it may be pointed out that the absence of linolenate and the low linoleate content mean that in any case the

<sup>53</sup> *Oil and Soap*, 1944, 21, 317; *A.*, 1945, II, 160.

<sup>54</sup> Cf. *Ann. Repts.*, 1943, 28, 235; 1944, 29, 242.

<sup>55</sup> *J.C.S.*, 1945, 445; *A.*, 1945, II, 309.

<sup>56</sup> *Ibid.*, 836; *A.*, 1946, II, 64.



main contributor to the oxygen uptake is oleate). Clearly a good deal still remains to be clarified in this extremely complex field. W. Treibs apparently still maintains that initial union of oxygen takes effect at a double bond, and in a recent paper<sup>57</sup> he has suggested that ethylene peroxides primarily produced may later be converted partially into hydroperoxides.

*Possible Ketonic Products of Autoxidation of Fats.*—It has been suggested that  $\alpha$ -diketonic compounds may be formed during oxidative rancidity, and colorimetric methods have been proposed by E. A. Prill<sup>58</sup> and by L. O'Daniel and L. B. Parsons<sup>59</sup> which are intended to give a measure of such compounds and thence to serve as tests for rancidity. H. Jasperson, R. Jones, and J. W. Lord<sup>60</sup> have applied these tests to diacetyl, 9 : 10-diketostearic acid, and to autoxidised groundnut oil and methyl linoleate, and spectroscopic examination of the colours produced has shown that, whilst the authentic  $\alpha$ -diketones respond successfully to the test, this grouping is not necessarily responsible for the colours obtained with the autoxidised fatty compounds. Some spectrometric studies of the oxidation of oleic, linoleic, linolenic, and conjugated triene acids, and their esters, by R. J. Holman, W. O. Lundberg, and G. O. Burr<sup>61</sup> shed further light on this question. These workers examined the spectra of autoxidised products from the above in presence of cold alkali (to produce enolisation), and compared the results with similar experiments on known compounds. They have stated that dihydroxystearic acids and oxidostearic acids cannot account for the absorption bands observed with the autoxidised products, and that ketolstearic and diketostearic acids, although showing bands at about 275  $m\mu$ ., do not account for the absorption in this region of autoxidised acids; on the other hand, they considered the increased absorption shown by autoxidised fats to be consistent with the presence of conjugated unsaturated systems containing carbonyl groups, or to conjugated polyenes formed by enolisation of these systems. The autoxidation products of linoleic acid were spectroscopically unlike those of oleic acid; until the autoxidation of monoethenoid derivatives has proceeded somewhat far, the products are relatively insensitive to alkali and there is only slight increase in absorption in an enolising medium.

In a further paper, Holman and Burr<sup>62</sup> have recorded similar observations on the absorption spectra of fats oxidised by lipoxidase; whilst linoleates, linolenates, etc. showed increased absorption near 230  $m\mu$ . and 270  $m\mu$ ., oleate failed to do so, from which the authors concluded that the monoethenoid derivatives were unattacked by lipoxidase. This conclusion appears invalid, since it is well established that the grouping

<sup>57</sup> *Ber.*, 1944, 77, [B], 69.

<sup>58</sup> *Oil and Soap*, 1942, 19, 107; *B.*, 1942, II, 375.

<sup>59</sup> *Ibid.*, 1943, 20, 72; *B.*, 1943, II, 255.

<sup>60</sup> *J.S.C.I.*, 1945, 64, 143; *C.*, 1945, 167.

<sup>61</sup> *J. Amer. Chem. Soc.*, 1945, 67, 1285, 1386, 1390; *A.*, 1946, I, 6.

<sup>62</sup> *Arch. Biochem.*, 1945, 7, 47; *A.*, 1945, III, 798.



$\cdot\text{C}:\text{C}\cdot\text{C}\cdot\text{C}:\text{C}\cdot$  is essential to the rapid development *ab initio* of conjugation during autoxidation. Their further conclusion that the products which give the increased intensities of absorption are probably conjugated ethenoid-carbonyl compounds also appears at present to rest on somewhat slender evidence.

### *Spectrographic Analysis of Drying Oils.*

Whilst the absorption in the far ultra-violet (210  $\text{m}\mu$ .) of unsaturated acids themselves (*i.e.*, without prior isomerisation by alkali) has been examined by R. H. Barnes, I. I. Rusoff, E. S. Miller, and G. O. Burr,<sup>63</sup> who have suggested that this mode of direct measurement may be utilisable in the determination of component acids, the determination of di-, tri-, and tetra-ene acids by standardised alkali isomerisation at 180° and measurement of the resulting intensity of absorption at 234, 268, 301, and 316  $\text{m}\mu$ ., originally proposed by Mitchell, Kraybill, and Zscheile,<sup>64</sup> is receiving much attention. The latter will undoubtedly rapidly overtake the use of thiocyanogen values in the analysis of polyethenoid fatty acids and fats.

B. W. Beadle and H. R. Kraybill<sup>65</sup> have given the following values for  $E_{1\text{ cm}}^{1\%}$  for the acids named after isomerisation with alkali at 180° for 25 minutes.

			234 $\text{m}\mu$ .	268 $\text{m}\mu$ .	301 $\text{m}\mu$ .	316 $\text{m}\mu$ .
Linoleic	..	..	860	—	—	—
Linolenic	..	..	609	532	—	—
Arachidonic	..	..	593	534	258	226

The same authors, with L. A. Stricker,<sup>66</sup> have stated that the method serves to distinguish lard (which contains small amounts of arachidonic acid) from hydrogenated vegetable fats. A. R. Baldwin and B. F. Daubert<sup>67</sup> have applied the method to the analysis of synthetic mixed glycerides containing linoleic and/or linolenic acid.

Direct spectrographic examination of the intensity of the band at 270  $\text{m}\mu$ . serves as a measure of the elæostearic acid content of an oil; R. T. O'Connor, D. C. Heinzelman, A. F. Freeman, and F. C. Pack<sup>68</sup> have given the values of  $E_{1\text{ cm}}^{1\%}$  at 270  $\text{m}\mu$ . for pure  $\alpha$ -elæostearic acid in different solvents as follows: 1698 (*isooctane*), 1686 (*cyclohexane*), 1834 (*ethanol*).

T. P. Hilditch, R. A. Morton, and J. P. Riley<sup>69</sup> have proposed a modification of the original Beadle and Kraybill technique for use in the detailed study of the component acids of drying oils. They prefer to calculate linolenic acid content from the result of alkali isomerisation

<sup>63</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 385; C., 1945, 28.

<sup>64</sup> *Ann. Repts.*, 1943, 28, 236.

<sup>65</sup> *J. Amer. Chem. Soc.*, 1944, 66, 1232; C., 1944, 180.

<sup>66</sup> *Oil and Soap*, 1945, 22, 50; B., 1945, II, 219; C., 1945, 182.

<sup>67</sup> *Ibid.*, 180; A., 1945, I, 327; C., 1945, 237.

<sup>68</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 467; C., 1945, 236.

<sup>69</sup> *Analyst*, 1945, 70, 68; A., 1945, II, 182; C., 1945, 102.



at 170° for 15 minutes, and linoleic acid after treatment at 180° for 60 minutes. The values of  $E_{1\text{cm}}^{1\%}$  found by these authors for individual unsaturated acids were as follows:

	Unisomerised.	Alkali-isomerised.	
		170°/15 mins.	180°/60 mins.
	268 m $\mu$ .	268 m $\mu$ .	234 m $\mu$ .
Linoleic .. ..	—	—	906
Linolenic .. ..	—	532	569
$\alpha$ -Elæostearic ..	1780	1690	197

With mixtures containing fairly large proportions of linolenic, linoleic, and oleic acids, and especially with those in which elæostearic acid is also present, the cumulative analytical errors may lead to uncertainty in the values obtained for oleic and saturated acids (determined from the iodine value of the mixed acids and/or by difference). T. P. Hilditch and J. P. Riley<sup>70</sup> have therefore recommended preliminary resolution of the mixed fatty acids of an oil into groups in which either linoleic and/or linolenic, or oleic and/or saturated, acids largely predominate. This can best be effected by systematic crystallisation of the mixed acids from acetone or ether at temperatures between -20° and -50°; for mixtures of low saturated acid content (as in most drying oils) low-temperature crystallisation is preferable to lead salt separation. Each separated group of acids is submitted to analysis spectrographically and/or by ester fractionation. The paper quoted deals with typical oils (sunflower seed, sesame, groundnut) in which oleic and linoleic acids are major components, concordant results being obtained either by ester fractionation or spectrographic analysis of the groups of acids separated by low-temperature crystallisation, or by ester fractionation following a lead salt separation. Separate studies covering modified schemes of analysis suitable for, respectively, fats containing linolenic as well as linoleic and oleic acids, and fats containing elæostearic acid as well as the non-conjugated unsaturated acids, are in progress.

#### *Individual Vegetable Drying Oils.*

*Linseed Oil.*—E. P. Painter<sup>71</sup> followed the development of fatty oil in growing flax seed in the seasons of 1941 and 1942, in both of which the proportion of free fatty acid and unsaponifiable matter in the oil decreased as the latter accumulated, whilst in 1942 the iodine value (135.4 eight days after flowering) increased to 198.1 twenty-seven days after flowering. The amounts of all the fatty acids in the seeds increased during oil deposition, except for a fall in linoleic acid; during ripening of the seed, the relative proportions of the component acids remained fairly constant in 1941, but in 1942 this was not the case, linolenic acid increasing at the expense of oleic as well as of linoleic acid.

<sup>70</sup> *J.S.C.I.*, 1945, 64, 204; *C.*, 1945, 243.

<sup>71</sup> *Arch. Biochem.*, 1944, 5, 337; *A.*, 1945, III, 333.



The spontaneous heating during storage of flaxseed and sunflower seed has been studied by H. R. Sallans, G. D. Sinclair, and R. K. Larmour,<sup>72</sup> who showed that it was conditioned by micro-organisms and not by respiratory processes, and that mould or bacterial growth is liable to set in if the moisture content of the stored seeds is sufficient to maintain a relative humidity of more than 74% in the interstitial air.

E. P. Painter,<sup>73</sup> after determining the component acids in 148 specimens of linseed oil from 8 varieties of flax grown in different U.S. districts, was able to deduce empirical relations whereby the respective proportions of oleic, linolenic, and saturated glycerides could be simply calculated from the iodine values of the oils. P. O. Powers<sup>74</sup> agreed with most of Painter's conclusions, and added a similar equation for calculating the linoleic content from the iodine value. H. R. Sallans<sup>75</sup> (with G. D. Sinclair) carried out similar determinations on 54 specimens of linseed oil (three varieties of flax) from 35 Canadian stations and gave a similar, but not identical, series of numerical formulæ correlating the content of each component acid with the iodine value of the oil. Since, in the writer's experience, use of both sets of formulæ can lead to results differing by 5 or more units per cent. for a given iodine value of a linseed oil, it would appear that these calculations are only of a very approximate order of accuracy. Their validity depends on a strictly linear relationship holding between the iodine and thiocyanogen values of linseed oils (the determinations being based on thiocyanometric analysis). It is doubtful whether this relationship is an exact one; at all events, component acid data obtained by the spectrographic method do not always accord with the values obtained by calculations using the above-mentioned empirical equations. Sallans has also discussed very fully the probable bearing of varietal and environmental difference on the average seed weight, oil content, and oil iodine value of Canadian linseed.

*Tung Oil.*—F. A. Johnson and H. M. Sell<sup>76</sup> have followed some of the changes which proceed in the tung kernel during germination of the seed; production of free fatty acids indicates that the glycerides are hydrolysed and the fatty acids converted into carbohydrates (reducing sugars and starch). R. S. McKinney and collaborators<sup>77</sup> have continued work on the influence of moisture content and other factors on the yield of oil by solvent extraction or by expression of tung fruits, including descriptions of laboratory technique for estimating the yield and quality of the oil. Since elæostearic acid and esters are altered by heat, J. C. Konen, E. T. Clocker, and R. P. Cox<sup>78</sup> have recommended that trielæostearin may be best prepared by treating equivalent amounts of methyl

<sup>72</sup> *Canad. J. Res.*, 1944, 22, F, 181; B., 1945, II, 83.

<sup>73</sup> *Oil and Soap*, 1944, 21, 343; B., 1945, II, 182; C., 1945, 172.

<sup>74</sup> *Ibid.*, 1945, 22, 52; B., 1945, II, 219.

<sup>75</sup> *Canad. J. Res.*, 1944, 22, F, 119, 132, 146; B., 1945, II, 181.

<sup>76</sup> *Plant Physiol.*, 1944, 19, 694; A., 1945, III, 645.

<sup>77</sup> *Oil and Soap*, 1944, 21, 328, 353; B., 1945, II, 142, 182; C., 1945, 173.

<sup>78</sup> *Ibid.*, 1945, 22, 57; B., 1945, II, 201.



elæostearate and triacetin with 0.15% of sodium methoxide at 60—100° in a vacuum.

### Marine Animal Oils.

Several reports have been made with reference to fish oils potentially available in the Dominions. The contents and vitamin-A potencies of the liver and visceral oils of a halibut species and of six species of flounders common in British Columbia have been investigated by B. H. Morton,<sup>79</sup> some of the fish comparing favourably with cod, dogfish, and other halibut in regard to vitamin potency and oil yield of the livers. The large-scale production of liver oils from some New Zealand fish (ling, groper, and some species of shark) has been described by M. M. Cunningham and C. Scott<sup>80</sup>; the livers of New Zealand ling, groper, and shark contain respectively about 25—40, 8—20, and 40—50% of oils, most of which are fairly, and sometimes very, rich in both vitamin-A and -D. The comprehensive studies of South African fish oil resources by W. S. Rapson, H. M. Schwartz, N. J. van Rensburg, *et al.*<sup>81</sup> have been continued and a number of further results communicated.<sup>82</sup> The yields and vitamin-A and -D contents of liver and visceral oils of the Cape hake (stockfish), kabeljou, geelbek, red gurnard, jacobever, sharks, rays, and many other fish have been recorded, with observations on the seasonal variations in the more abundant species. The body fats of the Cape John Dory and of other South African fish whose main fat depot is the flesh have been discussed separately, and the relative compositions of fats from different organs and depots of fish which possess diffuse systems of fat storage have been compared in regard to the mode and extent of the storage in different species. Full component acid analyses have been made of the following South African fish fats:

		Jacopever ( <i>Sebastichthys capensis</i> ).				Stockfish ( <i>Merluccius capensis</i> ). (Liver)
		Head.	Body.	Visceral.	Liver.	
Fat, iodine value	..	160.0	156.4	145.1	128.0	163.6
" unsaponifiable %		1.5	3.3	1.9	9.5	2.8
Acids (% wt.).						
Myristic	..	2.6	2.6	3.0	1.2	1.4
Palmitic	..	16.3	13.8	14.4	11.6	17.9
Stearic	..	2.1	1.8	2.2	3.9	1.9
Arachidic	..	0.8	0.2	0.1	0.4	0.5
Unsaturated	C <sub>14</sub> ..	0.9 (-2.0H)	2.3 (-2.0H)	1.9 (-2.0H)	0.6 (-2.0H)	0.4 (-2.0H)
"	C <sub>16</sub> ..	11.8 (-2.0H)	12.4 (-2.0H)	13.1 (-2.0H)	13.5 (-2.0H)	11.8 (-2.0H)
"	C <sub>18</sub> ..	30.3 (-3.0H)	28.5 (-2.4H)	30.6 (-2.5H)	46.3 (-2.3H)	32.6 (-3.3H)
"	C <sub>20</sub> ..	18.8 (-6.8H)	21.6 (-7.0H)	19.7 (-6.9H)	12.7 (-6.3H)	19.3 (-7.1H)
"	C <sub>22</sub> ..	15.5 (-9.6H)	16.8 (-9.5H)	12.3 (-9.2H)	7.5 (-8.7H)	12.0 (-9.0H)
"	C <sub>24</sub> ..	1.0 (-?H)	—	2.6 (-?H)	2.4 (-?H)	2.3 (-?H)

From the liver oil of the shark *Carcharodon carcharias* P. Baudart<sup>83</sup> has isolated small amounts, and deduced the constitution, of the following

<sup>79</sup> *Progr. Repts. Fish. Res. Bd. Canada, Pacific Stat.*, 1944, No. 61, 6; B., 1945, II, 115.

<sup>80</sup> *New Zealand J. Sci. Tech.*, 1944, 26, B, 21; B., 1945, III, 18.

<sup>81</sup> *Ann. Repts.*, 1944, 29, 245.

<sup>82</sup> *J.S.C.I.*, 1944, 63, 313, 367, 371; 1945, 64, 5, 7, 45, 47, 61, 114, 139, 140, 172; B., 1945, III, 18; II, 115, 184; A., 1945, III, 462; B., 1945, II, 244, 274.

<sup>83</sup> *Bull. Soc. chim.*, 1942, [v], 9, 733, 922; 1943, [v], 10, 440, 443; A., 1945, II, 183, 345.



acids:  $\Delta^{11:14}$ -eicosa- and  $\Delta^{11:14}$ -docosa-dienoic,  $\Delta^{8:11:14}$ -eicosa- and  $\Delta^{8:11:14}$ -docosa-trienoic, and  $\Delta^{8:12:16:20}$  (? 16:19 or 15:19)-docosa-tetraenoic.

*Glycerol Alkyl Ethers.*—L. A. Swain and B. H. Morton<sup>84</sup> have shown that dogfish and certain other elasmobranch liver oils from species in the Eastern Pacific frequently contain appreciable amounts of selachyl and related alcohols, amounting in different instances to from 6 to 31% of the oils.

E. Baer, L. J. Rubin, and H. O. L. Fischer<sup>85</sup> have synthesised *d*-selachyl alcohol ( $[\alpha]_D -4.35^\circ$ ) by interaction of the *p*-toluenesulphonate of oleyl alcohol with the sodium derivative of *l*-isopropylideneglycerol.

## COMPONENT ACIDS AND GLYCERIDES OF FATS: GENERAL.

### *Individual Fatty Acids etc.*

*Branched-Chain Saturated Acids.*—L. G. Ginger and R. J. Anderson<sup>86</sup> isolated from tubercle bacilli residues four crystalline optically active acids of the  $C_nH_{2n+2}O_2$  series containing 24, 25, 26, and 27 carbon atoms, the  $C_{26}H_{52}O_2$  acid having the properties of phthioic acid. N. Polgar and Sir R. Robinson<sup>87</sup> have described methods for synthesising polymethyl-substituted long-chain acids; such acids with three or more methyl substituents in the chain exhibit monolayer film properties similar to those of phthioic acid, which they therefore consider to possess an analogous structure; since oxidation of phthioic acid yields, *inter alia*, azelaic acid and an acid which is probably 6-methyldecoic acid, only two formulæ appear possible for the latter, and of these the authors prefer 3:13:19-trimethyltricosanoic acid. They effected a synthesis of the *dl*-form of this acid.

S. F. Velick<sup>88</sup> has inferred from X-ray study of the crystalline amides of tuberculostearic acid and *dl*-10-methylstearic acid that the natural acid is one of the enantiomorphic forms of the latter. The same author<sup>89</sup> has suggested, on similar evidence coupled with study of oxidation products, that phytomonic acid is probably 10- or 11-methylnonadecoic acid.

J. Cason and co-workers<sup>90</sup> have reported syntheses of 15-methyloctadecoic, 14-methyltetracosanoic, and other methyl- and ethyl-substituted long-chain acids.

*Normal Saturated Fatty Acids (Even-Numbered).*—The melting and solidification point curves for binary mixtures of adjacent pairs of fatty acids have been explored in the cases of hexoic—lauric acids by B. J. Grondal and D. A. Rogers,<sup>91</sup> and for triacontanoic( $C_{30}$ )—tetratriacontanoic

<sup>84</sup> *J. Fish. Res. Bd. Canada*, 1945, 6, 326; B., 1945, II, 307.

<sup>85</sup> *J. Biol. Chem.*, 1944, 155, 447; A., 1945, II, 35.

<sup>86</sup> *Ibid.*, 156, 443, 453; A., 1945, II, 107; C., 1945, 131.

<sup>87</sup> *J.C.S.*, 1945, 389; A., 1945, II, 307.

<sup>88</sup> *J. Biol. Chem.*, 1944, 154, 497; A., 1944, II, 319.

<sup>89</sup> *Ibid.*, 156, 101; A., 1945, II, 76.

<sup>90</sup> *J. Amer. Chem. Soc.*, 1944, 66, 1764; A., 1945, II, 76.

<sup>91</sup> *Oil and Soap*, 1944, 21, 303; A., 1945, I, 115; C., 1945, 102.



(C<sub>34</sub>) acids by H. A. Schuette, D. A. Roth, and R. M. Christenson.<sup>92</sup> Data for the solubilities (in cyclohexane, ethyl acetate, acetone, methanol, chloroform, and several other solvents) of fatty acids (and some binary mixtures thereof) from *n*-octoic to stearic have been recorded by C. W. Hoerr and A. W. Ralston.<sup>93</sup>

*New Syntheses of Oleic, Elaidic, and Linoleic Acids.*—Starting from 6-bromo-1-methoxyhexane and 1:2-dibromo-1-ethoxy-*n*-decane, P. Baudart<sup>94</sup> obtained by the Grignard reaction 1-methoxy- $\Delta^7$ -hexadecene, which by a series of further transformations was converted into the equilibrium mixture of 35% of oleic and 65% of elaidic acid. Subsequently, the same author prepared 1:2:4:5-tetrabromo-1:5-diethoxypentane from glutaraldehyde, and submitted it to Grignard condensations with magnesium *n*-amyl bromide and magnesium 6-methoxy-*n*-hexyl bromide, when 1-methoxy- $\Delta^{7:10}$ -hexadecadiene was obtained, and eventually converted as in the previous instance into a form of  $\Delta^{9:12}$ -octadecadienoic acid which yielded a tetrabromostearic acid, m.p. 77–78°, and was identical with the *trans-trans*-linoleic acid produced when ordinary linoleic acid is isomerised with selenium at 210°.

*Chemical Oxidation Products of Oleic Acid.*—M. Stoll and A. Rouve<sup>95</sup> have further studied the secondary reactions of the ozonides of oleic and similar acids whereby scission may occur in molecular fragments other than those produced by direct fission at the original double bond.

D. Swern, T. W. Findley, and J. T. Scanlan<sup>96</sup> have given conditions for the production of epoxy-compounds from oleic acid (or esters) and oleyl alcohol by perbenzoic and also by peracetic acid. The preparation and properties of twenty-three esters (some useful as plasticisers) of primary alcohols with the isomeric 9:10-dihydroxystearic acids have been described by D. Swern and E. F. Jordan.<sup>97</sup>

*Aleuritic Acid.*—In an attempt to synthesise this acid from 16-methoxy- $\Delta^9$ -hexadecenoic acid, P. C. Mitter, M. C. Sen-Gupta, and A. Bose<sup>98</sup> obtained a geometrically isomeric form of 9:10:16-trihydroxypalmitic acid, m.p. 125°.

*Alcohols of Carnauba Wax.*—S. D. Koonce and J. B. Brown<sup>99</sup> have separated almost pure specimens of the normal C<sub>28</sub>, C<sub>30</sub>, and C<sub>32</sub> saturated alcohols from carnauba wax by fractional distillation at 0.5 mm. pressure.

### Component Acids of Individual Fats.

*Advances in Analytical Technique.*—*Low-Temperature Crystallisation from Solvents.*—The value of this procedure in effecting preliminary

<sup>92</sup> *Oil and Soap*, 1945, 22, 107; A., 1945, I, 268.

<sup>93</sup> *J. Org. Chem.*, 1944, 9, 329; 1945, 10, 170; A., 1945, I, 23, 221.

<sup>94</sup> *Compt. rend.*, 1943, 217, 399; *Bull. Soc. chim.*, 1944, [v], 11, 336; A., 1945, II, 182, 308.

<sup>95</sup> *Helv. Chim. Acta*, 1944, 27, 950; A., 1944, II, 318.

<sup>96</sup> *J. Amer. Chem. Soc.*, 1944, 66, 1925; 1945, 67, 412; A., 1945, II, 76, 220.

<sup>97</sup> *Ibid.*, 1945, 67, 902; A., 1945, II, 308.

<sup>98</sup> *J. Indian Chem. Soc.*, 1944, 21, 295; A., 1945, II, 139.

<sup>99</sup> *Oil and Soap*, 1944, 21, 231; B., 1945, II, 24.



resolutions of the mixed fatty acids of liquid vegetable oils,<sup>70</sup> and its advantages in these and other instances over the older method of lead salt separation, have been dealt with earlier in this Report (p. 283). The method has also been recently used by E. L. Jack and J. L. Henderson<sup>100</sup> in the study of the component acids of cow milk fat, which they thus separated into five groups prior to ester fractionation, and by W. S. Singleton, M. Lambou, and A. E. Bailey,<sup>101</sup> who have given data for the resolution of raw or hydrogenated cottonseed oil mixed acids into fractions by the use of acetone or light petroleum at temperatures between 2° and -26°, the components of each fraction being evaluated from iodine and thiocyanogen values.

*Ester Fractionation.*—A number of the salient factors in the design and operation of laboratory fractionation columns for separation of higher fatty esters has been re-discussed by F. A. Norris and D. E. Terry,<sup>102</sup> who indicate that more effective separation is attainable with a Podbielniak column than with a Whitmore-Lux column; the authors have also given precise data for the boiling points of methyl myristate, palmitate, stearate, oleate, and linoleate at 1, 2, 5, 10, and 20 mm. pressure, and for the latent heats of vaporisation of the esters over the pressure range 1—20 mm. The vapour pressure curves, boiling points, and decomposition temperatures of these esters and of methyl *n*-hexoate, *n*-octoate, *n*-decoate, and laurate have been determined by P. M. Althouse and H. O. Triebold.<sup>103</sup> Fractional distillation of mixtures of known compositions of methyl esters of saturated (lauric—stearic), oleic, linoleic, and linolenic acids, followed by spectrographic determination of linoleate and linolenate and determination of iodine value and saponification equivalent in each ester fraction, has afforded A. R. Baldwin and H. E. Longenecker<sup>104</sup> calculated compositions which agreed satisfactorily with those of the original mixtures.

*Animal Body Fats.*—Guinea-pig body fat was found by A. R. Baldwin and H. E. Longenecker<sup>105</sup> to contain as component acids: lauric 1.1, myristic 5.3, palmitic 19.4, stearic 5.7, tetradecenoic 0.8, hexadecenoic 2.1, oleic 36.2, octadecadienoic 18.8, octadecatrienoic 1.2, eicosatetraenoic 2.4, and other unsaturated C<sub>20-22</sub> acids 7.0% (wt.).

Puma (*Felix concolor*) body fat was found by F. Giral<sup>106</sup> to have component acids: myristic 1.3, palmitic 22.4, stearic 26.9, arachidic 3.7, hexadecenoic 12.6, oleic 26.2, octadecadienoic 2.3, unsaturated C<sub>20</sub> acids 4.6% (wt.).

*Vegetable Fats.*—The glycerides in rape (*Brassica napus*) leaves contain,

<sup>100</sup> *J. Dairy Sci.*, 1945, **28**, 65; *J. Nutrition*, 1945, **30**, 175; *A.*, 1945, III, 869; *C.*, 1946, 41.

<sup>101</sup> *Oil and Soap*, 1945, **22**, 168; *B.*, 1945, II, 345.

<sup>102</sup> *Ibid.*, 41; *A.*, 1945, II, 219; *C.*, 1945, 167.

<sup>103</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 605; *A.*, 1945, II, 36; *C.*, 1945, 19.

<sup>104</sup> *Oil and Soap*, 1945, **22**, 151; *C.*, 1945, 237.

<sup>105</sup> *Arch. Biochem.*, 1944, **5**, 147; *A.*, 1945, III, 247.

<sup>106</sup> *J.C.S.*, 1945, 112; *A.*, 1945, III, 452.



in addition to a large amount of linolenic acid and some hexadecenoic acid, about 3—4% of hexadecatrienoic acid, according to crystallisation and ester fractionation studies by F. B. Shorland.<sup>107</sup>

The fat in the thin brown testa of the palm kernel (*Elais guineensis*) contains more oleic and linoleic acids, and less lauric acid, than that in the endosperm; H. A. Carsten, T. P. Hilditch, and M. L. Meara<sup>108</sup> have given the following figures for the component acids of endosperm and corresponding testa respectively; caprylic 3.9, 0.6; capric 6.3, 4.4; lauric 51.2, 35.7; myristic 17.5, 16.0; palmitic 6.5, 10.7; stearic 2.0, 1.5; arachidic 0.5, —; hexadecenoic 0.4, 0.1; oleic 10.5, 26.0; linoleic 1.2, 5.0% (wt.).

The component acids (% wt.) of a number of seed fats (additional to others which have been mentioned in earlier sections of this Report) have been reported as in the annexed table.

	Palmitic.	Stearic.	Oleic.	Linoleic.	Linolenic.
<i>Acacia albida</i> <sup>109</sup>	←20*→	—	45	33	—
<i>A. arabica</i> <sup>109</sup>	←22*→	—	42	36	—
<i>A. mellifera</i> <sup>109</sup>	←35*→	—	43	22	—
<i>A. seyal</i> <sup>109</sup>	←26*→	—	36	38	—
<i>A. sieberiana</i> <sup>109</sup>	←25*→	—	31	44	—
<i>A. verec</i> <sup>109</sup>	←24*→	—	38	38	—
<i>Allbizia lebbek</i> <sup>109</sup>	←29*→	—	43	28	—
Cat-tail ( <i>Typha latifolia</i> ) <sup>110</sup>	←20.5→	—	15.1	53.5	—
<i>Hyoscyamus niger</i> <sup>111</sup>	6.5†	1.6	35.2	56.4	—
Niger seed <sup>112</sup>	←9.6→	—	16.3	72.4	1.7
Stillingia seed <sup>112</sup>	←7.3→	—	4.5	66.8	21.4
Tobacco seed <sup>113</sup>	7	3	15	75	—†
<i>Vernonia anthelmintica</i> <sup>114</sup>	7.0	5.9	5.7	9.6	—§
Wheat germ <sup>115</sup>	←15.5→	—	25.5	52.6	6.3

\* Including respectively, 2.2, 1.2, 4.4, 2.9, 4.4, 3.1, and 3.1% of saturated C<sub>20</sub>–C<sub>21</sub> acids.

† Also 0.3% of myristic acid.

‡ Average composition of 12 samples.

§ Also 7.4% of myristic acid, 2% of resin, and 62.4% of vernolic (? 11-hydroxy- $\Delta^9$ -octadecenoic) acid.

**Tall Oil.**—Six specimens of tall oil produced in the southern United States and examined by R. H. Anderson and D. H. Wheeler<sup>116</sup> contained from 26 to 61% of fatty acids, with from 46 to 32% of rosin acids. The components of the fatty acids of all the samples were similar, and averaged saturated (chiefly palmitic) acid 7%, oleic 45% (including up to 1% of hexadecenoic acid), and “linoleic” acid 48% (including about 11% of

<sup>107</sup> *Nature*, 1945, 156, 269.

<sup>108</sup> *J.S.C.I.*, 1945, 64, 207; B., 1945, II, 306.

<sup>109</sup> D. N. Grindley, *J.S.C.I.*, 1945, 64, 152; B., 1945, II, 243.

<sup>110</sup> H. A. Schuette and L. Gagneron, *A.O.C.S.*, 19th Autumn Meeting, Chicago, 1945.

<sup>111</sup> S. P. Pathak, B. G. Gunde, and N. N. Godbole, *Indian Soap J.*, 1944, 9, 5.

<sup>112</sup> C. R. Pye, *Paint Tech.*, 1945, 10, 113; B., 1945, II, 273.

<sup>113</sup> R. W. Riemenschneider, R. M. Speck, and E. G. Beinhart, *Oil and Soap*, 1945, 22, 120; B., 1945, II, 346.

<sup>114</sup> N. L. Vidyarthi, *Patna Univ. J.*, 1945, 1, 51; A., 1945, II, 308.

<sup>115</sup> S. B. Radlove, *Oil and Soap*, 1945, 22, 183; B., 1945, II, 345.

<sup>116</sup> *Ibid.*, 137; B., 1945, II, 306.



conjugated octadecadienoic acid, probably formed by the action of heat and alkali during the cooking of the pulp from which the tall oil originated). Linolenic acid was not observed. The potential industrial value of tall oil has been further discussed by W. H. Jennings,<sup>117</sup> who states that it can be resolved by vacuum distillation into fatty acids containing 5% of rosin acids, rosin acids containing 5% of fatty acids, and residual tall oil pitch. According to Jennings the fatty acids include oleic 17—45%, linoleic 50—80%, and linolenic 5—15%.

*Natural and Synthetic Mixed Glycerides.*

C. and A. Venkatarao and M. Narasingarao<sup>118</sup> have determined the component glycerides of a specimen of Indian tobacco seed oil to be oleodilinolein 35%, palmito- (18%) and stearo-cleclinoleins (11%), palmitcdilinolein 9%, trilinolein 7%, and dicleclinolein 7%, with minor amounts of myristo-unsaturated glycerides and of stearodilinolein.

M. L. Meara<sup>119</sup> has published the first of a series of studies dealing with the isolation in a state of purity of individual mixed glycerides (or their corresponding saturated derivatives produced by low-temperature hydrogenation) from a number of natural fats, and the thermal examination of the melting and transition points of their polymorphic forms. The data for natural oleodistearin from six different seed fats in which it is a major component showed identity in each instance with  $\beta$ -olecdistearin, and differences from the unsymmetrical  $\alpha$ -oleodistearin. Oleopalmitostearin from cacao butter, palmitodioleins from pig fat, and palmito-oleolinoleins from cottonseed oil were converted into the corresponding palmitodistearins, when the thermal data for the products obtained coincided in each case with those for  $\beta$ -palmitodistearin and differed from those of the unsymmetrical  $\alpha$ -palmitodistearin.

The work of the Daubert-Baldwin-Longenecker school on the characterisation of synthetic mixed glycerides by thermal and X-ray data has been continued and extended. B. F. Daubert and A. R. Baldwin<sup>120</sup> have described the preparation and properties of  $\alpha$ -linoleo-disaturated and of  $\alpha$ -monosaturated-dilinoleo-glycerides for members of the even-numbered saturated group from octoic to stearic. B. F. Daubert and T. H. Clarke<sup>121</sup> have given a detailed account of the apparatus and thermal technique used, with a review of their melting and transition point data for synthetic  $\alpha$ -oleo-disaturated glycerides,  $\alpha$ -monosaturated dioleins, and  $\beta$ -monoglycerides of the saturated series. B. F. Daubert<sup>122</sup> has improved the preparation of  $\alpha\alpha'$ -benzylideneglycerol and its conversion, ultimately, into its  $\beta$ -oleate and  $\beta$ -elaidate, both of which yield  $\beta$ -monostearin on hydrogenation (palladium in alcohol).

<sup>117</sup> *Paper Trade J.*, 1945, **120**, *TAPPI Sect.*, 185; *B.*, 1945, **II**, 244.

<sup>118</sup> *J. Indian Chem. Soc.*, 1944, **21**, 249; *A.*, 1945, **III**, 496.

<sup>119</sup> *J.C.S.*, 1945, **22**, 23; *A.*, 1945, **II**, 107.

<sup>120</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1507; *A.*, 1945, **II**, 35.

<sup>121</sup> *Oil and Soap*, 1945, **22**, 113; *A.*, 1945, **I**, 240; *C.*, 1945, 172.

<sup>122</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 1033; *A.*, 1945, **II**, 309.



The polymorphism of simple synthetic saturated glycerides (trilaurin to tristearin) has been re-examined by E. S. Lutton,<sup>123</sup> who differs on some points (notably the concept of the glass or smectic state as an individual " $\gamma$ " form) from the earlier conclusions of Malkin.<sup>124</sup>

#### METHODS OF TESTING AND ANALYSIS.

The use of adsorption on a column of aluminium oxide in the determination of fats in admixture with fatty acids (*e.g.*, soap stock "acid oils") and of unsaponifiable matter in fats has been recommended by N. D. Sylvester, A. N. Ainsworth, and E. B. Hughes,<sup>125</sup> who have given full details of procedure. In the first method, fatty acids are left on the column while neutral fat passes into the eluate. In determining unsaponifiable matter the fat is first hydrolysed according to the S.P.A. method and the soap solution extracted with ether; at this point the ether extract is washed with dilute acid and then passed through the adsorption column to remove all fatty acid liberated from traces of soap in the ether. This procedure gives closely similar results to, and is much shorter than, the laborious washings of the ether solution necessary in the older methods. Further reports are promised on similar application of the adsorption method in the isolation and determination of the fully saturated glyceride contents of fats.

A volumetric method for determining monoglycerides in fats, depending on their oxidation with periodic acid, has been proposed by W. D. Pohle, V. C. Mehlenbacher, and J. H. Cook.<sup>126</sup>

*Dilatometric and Thermal Properties of Fats and Fatty Oils.*—Apparatus and technique suitable for measuring the dilatometric behaviour of fats between 0° and their melting points, and for carrying out calorimetric studies (melting point, specific heats, latent heats of fusion) of fats, have been described in a series of papers by A. E. Bailey and co-workers<sup>127</sup>; precise thermal data have been presented for cottonseed oil and a number of hydrogenated cottonseed oils.

*Halogen Values etc.*—M. D. Voth<sup>128</sup> has found that the Hanus iodine value of surplus oil drained from canned fish is not materially affected by oil exuded from the fish flesh, and that it can therefore be used as a criterion of the packing oil in regard to possible adulteration of the latter (*e.g.*, adulteration of olive oil used in packing).

G. K. Crowell<sup>129</sup> has given details of a modified hexabromide method for the detection of linolenic acid in edible animal fats, adapted to the qualitative detection of admixed horse fat (which contains appreciable proportions of linolenic glycerides).

<sup>123</sup> *J. Amer. Chem. Soc.*, 1945, 67, 524; A., 1945, II, 267.

<sup>124</sup> *Ann. Repts.*, 1934, 19, 433.

<sup>125</sup> *Analyst*, 1945, 70, 295; C., 1945, 243.

<sup>126</sup> *Oil and Soap*, 1945, 22, 115; C., 1945, 172.

<sup>127</sup> *Ibid.*, 1944, 21, 251, 254, 293, 297, 300; B., 1945, II, 113, 114; C., 1945, 108.

<sup>128</sup> *J. Assoc. Off. Agric. Chem.*, 1944, 27, 455; C., 1945, 41.

<sup>129</sup> *Ibid.*, 448; C., 1945, 40.



By suitable storage in dark bottles, F. A. Norris and R. J. Buswell<sup>130</sup> have been able to preserve Wijs iodine reagent unaltered (at ordinary temperatures) for over eighteen months. Measures to conserve the stability of this reagent in the tropics have been discussed by R. Child.<sup>131</sup>

Further precautions leading towards the preparation of thiocyanogen reagent of improved stability and applicability have been outlined by M. G. Lambou and F. G. Dollear,<sup>132</sup> the principal features, in addition to rigorous maintenance of anhydrous conditions, being the use of a mixture of 25% of carbon tetrachloride and 75% of glacial acetic acid in place of 100% acetic acid in preparing the reagent, the use of finely powdered, dry potassium iodide, and of double the amount of potassium iodide necessary to react with the thiocyanogen in the control solution.

*Reports of Analytical Committees etc.*—The following reports and recommendations of the American Oil Chemists' Society may be noted: collaborate tests on thiocyanogen values and on the Halphen test for detecting traces of cottonseed oil in other oils,<sup>133</sup> bleaching tests for oils,<sup>134</sup> oil content of soya beans,<sup>135</sup> various tests for sampling nuts and seeds, and for soap analysis,<sup>136</sup> colorimetric tests with special reference to oil-bleaching tests,<sup>137</sup> refining of expressed, expelled, and extracted oils,<sup>138</sup> thiocyanogen values, stability (oxidation) tests, hexabromide tests and determination of unsaponifiable matter in fatty oils,<sup>139</sup> provisional specified characteristics for neatsfoot oil, beef tallow, North American lard, babassu fat, Chinese vegetable tallow, and other fats.<sup>140</sup>

<sup>130</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 417; C., 1945, 17.

<sup>131</sup> *Ibid.*, 1945, **17**, 530; C., 1945, 242.

<sup>132</sup> *Oil and Soap*, 1945, **22**, 226; C., 1946, 22.

<sup>133</sup> *Ibid.*, 1944, **21**, 143; C., 1944, 171.

<sup>134</sup> *Ibid.*, 196; 1945, **22**, 153; C., 1944, 171.

<sup>135</sup> *Ibid.*, 1944, **21**, 305; 1945, **22**, 141; C., 1945, 118.

<sup>136</sup> *Ibid.*, 1944, **21**, 310; C., 1945, 118.

<sup>137</sup> *Ibid.*, 360; 1945, **22**, 13, 22; C., 1945, 201, 172.

<sup>138</sup> *Ibid.*, 1945, **22**, 34, 156; C., 1945, 243.

<sup>139</sup> *Ibid.*, 101; C., 1945, 243.

<sup>140</sup> *Ibid.*, 160; B., 1945, II, 306.



# PLASTICS.

BY MEMBERS OF THE PLASTICS GROUP.

## THERMOPLASTIC SYNTHETIC RESINS.

BY MERVYN G. CHURCH, PH.D., B.Sc., A.R.I.C.,

*Ministry of Supply.*

THE period reviewed in this report closed as the veil was being lifted on many war-time developments which had previously been classified as secret. While this report will not contain much information on these advances, it may be expected that the ensuing year will provide much interesting information on British, American, and continental progress.

During the past year the theory of polymerisation reactions has been advanced by several interesting papers.

The effect of oxygen on the polymerisation of vinyl derivatives has been studied by C. E. Barnes<sup>1</sup> in an effort to account for the inhibiting action of oxygen in the photopolymerisation of vinyl monomers. He has suggested that the activated molecules formed by irradiation with ultra-violet light react preferentially with oxygen to form a peroxide and that this peroxide complex is capable of activating other molecules of monomer which also preferentially form peroxides. From the results of controlled experiments on the polymerisation of methyl methacrylate and vinyl acetate, in the presence and absence of oxygen, in which the amounts of peroxide and polymer formation were measured, the author has concluded that his suggestion is confirmed and that a similar inhibition by oxygen occurs in thermal polymerisation.

A study has been made of the emulsion polymerisation of styrene by E. W. Montroll.<sup>2</sup> In the polymerisation of a water emulsion of styrene he has concluded that the inhibition period which occurs after the addition of the water-soluble catalyst is due to the destruction of impurities in the emulsion which inhibit the polymerisation reaction. A further conclusion is that the polymerisation reaction probably occurs at the water-styrene interface, for since the catalyst is insoluble in styrene, the reaction cannot occur inside the styrene globules, and since the reaction rate decreases with increasing globule size, and therefore decreasing interface area, the reaction probably does not occur in the water phase. Experimental data show that the inhibition period increases with initial mean radius and that the rate curves are essentially parallel during the intermediate stages of the polymerisation. The author bases his explanations of these observations on the assumption that the impurity causing

<sup>1</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 217; A., 1945, II, 219.

<sup>2</sup> *J. Chem. Physics*, 1945, **13**, 337.



the initial inhibition is contained in the styrene globules and is destroyed by the catalyst only after diffusing into the water phase. From a mathematical treatment of these explanations the author has derived curves bearing a close resemblance to the experimental curves.

F. R. Mayo and F. M. Lewis<sup>3</sup> have studied the copolymerisation of styrene and methyl methacrylate. Basing their consideration on the assumption that the copolymerisation involves the reaction of the two monomers with the two corresponding activated complexes, they have shown that it is possible to express the composition of the copolymer formed as a function of the initial concentrations of the monomer, of the conversion, and of constants representing each pair of monomers. Each of these constants is the ratio of the rate constants for the reaction of one activated molecule with the corresponding monomer and with the other monomer. A series of experimental copolymerisation reactions between the two monomers in the presence of various added materials, including solvents and in the presence and absence of benzoyl peroxide, has shown that the constants are independent of these variables. In the system studied both styrene and methyl methacrylate show a preference to react with one another rather than with molecules of their own type. The equation developed permits the quantitative comparison of the rates of reaction of a series of monomers with another monomer under certain conditions.

The structure of copolymers has also received the consideration of F. T. Wall,<sup>4</sup> who, from the same basis, has derived equations in which the fractions, of the total bonds, of bonds of any one type (for example, styrene-methyl methacrylate, styrene-styrene, and methyl methacrylate-methyl methacrylate) and the lengths in molecules of groups of certain types of molecules (for example, styrene) in a polymeric chain are expressed in terms of the constants and the initial monomeric compositions. The equation is used to derive values of the fractions and group lengths for a number of examples in which typical values for the constants and initial composition are taken.

W. H. Stockmayer<sup>5</sup> has derived expressions for the distribution of chain lengths in copolymerisation reactions and for the instantaneous distribution of chain compositions. The former expression agrees with that for the size distribution in pure polymers, while the latter should be used only for copolymers of low conversion.

In the study of the heat of polymerisation, L. K. J. Tong and W. O. Kenyon<sup>6</sup> have applied the use of an isothermal calorimeter to the polymerisation of methyl methacrylate. Several experimental results are recorded using various amounts of benzoyl peroxide as catalyst, the calorimeter liquid being carbon tetrachloride and, in one case, toluene.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1594; A., 1945, I, 32.

<sup>4</sup> *Ibid.*, 2050; A., 1945, I, 134.

<sup>5</sup> *J. Chem. Physics*, 1945, **13**, 199; A., 1945, I, 264.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 1278; A., 1945, I, 309.



Precautions were taken in the design of the reaction tube to allow for the poor thermal conductivity of the monomer and polymer. The results obtained show good agreement, although the average heat of polymerisation,  $13.0 \pm 0.2$  g.-cal. per mol., is rather higher than that obtained by other workers.

X-Ray data for a number of vinyl and other olefinic polymers have been examined by M. L. Huggins,<sup>7</sup> who has concluded that the data indicate in most cases that the polymeric chains are in the form of a regular spiral which is unidirectional in each chain and which has uniform pitch. W. T. Astbury<sup>8</sup> has also examined X-ray data of polymers. He has stated that for each polymer there is a temperature at which an oriented polymer, as shown by X-rays, contracts and returns to the amorphous state.

J. Rehner, jun.,<sup>9</sup> has examined the work of T. Zvetkov and E. Frisman<sup>10</sup> on the shape of molecules of polyisobutene dissolved in hydrocarbon solvents. These workers had shown that the birefringence of polyisobutene solutions depended on the velocity gradient and that the curve obtained when birefringence is plotted against velocity gradient contained a break at a value of the velocity gradient which appeared to be characteristic of the polymer. They had provided an explanation of their curve based on a theory developed by J. Frenkel<sup>11</sup> which assumes that the normally coiled molecule becomes rod-like at the critical velocity gradient above which rupture of the polymer occurs. Using a polyisobutene sample, the molecular weight of which had been determined by the Staudinger equation, these authors had calculated the critical velocity gradient and had found it to agree well with the corresponding curve. The results of Zvetkov and Frisman are criticised by Rehner on the grounds that the Staudinger equation is not applicable to polyisobutene solutions and that if the molecular weight of the sample had been determined by osmometry the agreement between the observed and calculated values of the critical velocity gradient would not have been obtained. The equation derived by Zvetkov and Frisman is also criticised on the basis that in its derivation the assumption is made that the extension of the link undergoing rupture obeys Hooke's law, which is considered to be inapplicable to this process.

T. Alfrey and P. Doty<sup>12</sup> have considered the effect of the heat of mixing and the temperature-dependence of the osmotic pressure on the existing theories for dilute solutions of polymers. Assuming a solvent-solute interaction they have derived an expression for the configuration partition function containing a factor representing this interaction. From this

<sup>7</sup> *J. Chem. Physics*, 1945, 13, 37; A., 1945, I, 135.

<sup>8</sup> *Chem. and Ind.*, 1945, 114; B., 1945, II, 187.

<sup>9</sup> *J. Chem. Physics*, 1945, 13, 450; A., 1946, I, 85.

<sup>10</sup> *Acta Physicochim. U.R.S.S.*, 1945, 20, 61; A., 1945, I, 246.

<sup>11</sup> *Ibid.*, 1944, 19, 51; A., 1945, I, 59.

<sup>12</sup> *J. Chem. Physics*, 1945, 13, 77; A., 1945, I, 167.



expression, equations have been derived for the partial molar thermodynamic quantities and for osmotic pressure. The equation for the osmotic pressure has been plotted for a series of arbitrary molar constants and the authors claim that the temperature-dependence concords with that expected from classical thermodynamics. In the equation for the partial molar heat of mixing the dependence on concentration appears to agree with results obtained by G. Gee and L. R. G. Treloar.<sup>13</sup>

The thermodynamics of high polymer solutions has also been the subject of a paper by R. L. Scott and M. Magat.<sup>14</sup> In this paper the free energy of mixing of a polymer with a range of chain lengths and a mixture of solvents has been considered. From the work of Huggins,<sup>16</sup> which dealt with the free energy of mixing of a polymer of uniform chain length and a single solvent, the authors have derived expressions for the partial molar entropies of the solvent and polymer which show that the partial molar entropy of the solvent is dependent on the number average molecular weight but not on the molecular weight distribution, whereas that of the polymer is dependent on both. From these expressions equations have been derived for partial molar free energies in the cases of simple and mixed solvents. In a subsequent paper R. L. Scott<sup>15</sup> has applied the equations derived in the first paper to problems connected with the solubility and fractionation of polymers.

The influence of the shape of dissolved molecules on viscosity, sedimentation, and diffusion has been studied by R. Simha,<sup>17</sup> who has derived expressions connecting these properties. The equation for viscosity contains a factor representing the degree of straightening out of the ideal coil form of the molecule, and values of this factor are given for a number of polymeric molecules. Similar expressions have been derived for sedimentation and diffusion. The factors obtained appear to differ from those deduced by J. J. Hermans<sup>18</sup> but Simha has stated that the value differs as the solvent is varied.

A modified osmometer suitable for the study of high polymer solutions that tend to form stable foams has been described by R. H. Wagner.<sup>19</sup>

The use of light scattering of polymer solutions as a means for determining molecular weights has been examined by P. M. Doty, B. H. Zimm, and H. Mark.<sup>20</sup> By measurements of the intensities of light scattered and refractive indices of solutions of various concentrations, weight average molecular weights have been determined which are compared with molecular weights of the same samples determined by osmometry.

Light scattering has been used by D. R. Morey and J. W. Tamblyn<sup>21</sup>

<sup>13</sup> *Trans. Faraday Soc.*, 1942, **38**, 147.

<sup>14</sup> *J. Chem. Physics*, 1945, **13**, 172; A., 1945, **1**, 225.

<sup>15</sup> *Ibid.*, 178; A., 1945, **1**, 225.

<sup>16</sup> *Ann. New York Acad. Sci.*, 1942, **43**, 1.

<sup>17</sup> *J. Chem. Physics*, 1945, **13**, 188; A., 1945, **1**, 223.

<sup>18</sup> *Kolloid Z.*, 1944, **106**, 22; A., 1945, **1**, 26.

<sup>19</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 520; C., 1945, 82.

<sup>20</sup> *J. Chem. Physics*, 1945, **13**, 159; C., 1945, 200.

<sup>21</sup> *J. Appl. Physics*, 1945, **16**, 419; A., 1946, **1**, 46.



in measuring the distribution of molecular weights. The amount of light scattered during the progressive precipitation of a polymer from a solution by the addition of a non-solvent was used as a measure of the weight precipitated. From the results obtained a graph of the molecular weight distribution has been derived which is compared with a curve obtained gravimetrically for similar samples of cellulose acetate butyrate.

The second-order transition point of polymers has been further studied by R. F. Boyer,<sup>22</sup> who has examined the effect of the ratio of the two components of a copolymer on the transition temperature. He has found that the transition temperature increases with the polarity of the group in the side-chain. Thus, in the system styrene-butadiene, the transition temperature rises as the proportion of styrene is increased. By increasing the amount of cross linking in a polymer or copolymer the transition point can also be raised.

P. M. Doty, W. H. Aiken, and H. Mark<sup>23</sup> have described an apparatus suitable for measuring rapidly rates of water vapour transmission through films. The method and equations derived permit the calculation of the permeability coefficient, the diffusion coefficient, and the solubility coefficient of water vapour for the film under examination and values for these coefficients are given for a number of polymers. The authors consider that the permeability is inversely proportional to film thickness except when the material of the film is hydrophilic or capable of absorbing much water. The current theories for the diffusion of gases through films have been reviewed by the authors, who have postulated a new theory based on a suggestion that the "inner surface" which some high polymers possess involves narrow crevices which contain numbers of centres of high absorptive power, and that molecules of water vapour diffuse through the material by moving from one centre to another.

The impact strength of plastics has been studied by several authors. M. E. Marks<sup>24</sup> has measured the impact strengths of a series of cross-linked allyl polymers by means of falling weights on unnotched specimens, and has compared the results with values calculated from flexural tests. Some agreement was obtained with the allyl derivatives. D. R. Morey<sup>25</sup> has presented a valuable review of existing theories for, and methods of, determining impact strength. He has used mechanical models to illustrate the factors affecting impact strength which he has attempted to relate to molecular structure. He considers that brittleness occurs when the secondary bonds in a material are similar in relaxation time and extensibility. When dissimilar the material tends to be tougher and less notch-sensitive.

Tensile strengths of a variety of plastics, of both thermoplastic and thermosetting types, have been examined by R. T. Schwartz,<sup>26</sup> who has

<sup>22</sup> *Canad. Chem.*, 1944, **28**, 528; *B.*, 1945, **II**, 25.

<sup>23</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 686; *C.*, 1945, 73.

<sup>24</sup> *Mod. Plastics*, 1945, **22**, No. 6, 153.

<sup>25</sup> *Ind. Eng. Chem.*, 1945, **37**, 255; *B.*, 1945, **II**, 187.

<sup>26</sup> *Mod. Plastics*, 1945, **23**, No. 1, 194.



studied and recorded values for the variation of tensile strength and elongation with temperature. The relative temperature-stability of a similar range of plastics has been investigated by J. A. Sauer, F. A. Schwertz, and D. L. Worf,<sup>27</sup> who have presented values for the distortion temperatures which, they consider, indicate that all thermosetting plastics should be capable of post-forming.

The electrical properties of plastics have been considered from a theoretical aspect by L. Hartshorn,<sup>28</sup> who has indicated the relationship between the dielectric properties and molecular structure based on the theories of Maxwell and Debye.

The interaction of plasticisers and polymers has been the subject of an interesting paper by E. M. Frith,<sup>29</sup> in which the measurement of this interaction is used as a means of determining the degree of compatibility. The viscosities of polymers in dilute solutions in the plasticiser or in solvents containing the plasticiser were measured, and the viscosity curves were used to determine polymer-plasticiser interactions and to obtain from them a measure of the compatibilities. The systems polyvinyl chloride and polyvinyl acetate are used as examples, and experimental results obtained for these systems are shown to agree with the known compatibility properties.

H. W. Thompson and P. Torkington<sup>30</sup> have made a study of the infrared spectra of polymers and have shown that this form of examination can assist in the elucidation of structural problems. A number of spectra for polymers of high molecular weight are given, and the structures of the polymers are discussed on the basis of the evidence provided by these spectra.

Analytical aspects of plastics have been the subject of papers by H. Barron<sup>31</sup> and T. P. G. Shaw,<sup>32</sup> who have put forward schemes for identifying resins.

#### POLYACRYLATES.

While the demand still exists for an aircraft glazing material having greater heat- and scratch-resistance than the present forms of polymethyl methacrylate, this type of material still holds the field for all applications in which shapes having double curvature are required. Cross-linked resins have not so far been successful in gaining a foothold in this field owing probably to the greater difficulty of forming materials of this kind and their tendency to shatter in a brittle manner on high-velocity impact. There seems to be a tendency to use laminated glass where possible in aircraft and the solution of this problem may lie ultimately in the development of a technique for producing laminated glass with double

<sup>27</sup> *Mod. Plastics*, 1945, 22, No. 7, 153; B., 1945, II, 382.

<sup>28</sup> *Brit. Plastics*, 1945, 17, 99, 186.

<sup>29</sup> *Trans. Faraday Soc.*, 1945, 41, 90; A., 1945, I, 163.

<sup>30</sup> *Ibid.*, 246; A., 1945, I, 183.

<sup>31</sup> *Brit. Plastics*, 1945, 16, 339, 460; 17, 56; C., 1945, 109.

<sup>32</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 541; C., 1945, 29.



curvatures or in the development of suitable cross-linked resins employed in a laminated form.

Claims have been made by the Pittsburgh Plate Glass Co.<sup>33</sup> for glazing materials, having improved abrasion- and solvent-resistance, comprising a sheet of polymer such as polymethyl methacrylate coated with a thin layer of an infusible polymer such as the polymer of glycol dimethacrylate or allyl methacrylate.

The medical profession appears to have taken a considerable interest in the use of polymers of methyl methacrylate. Accounts have appeared describing the use of acrylic resins for the production of artificial eyes,<sup>34</sup> and as an observation window in skulls,<sup>35</sup> while denture bases<sup>36</sup> from acrylates continue to be developed. A general review of these developments has been given by A. MacGowan.<sup>37</sup>

The preparation of acrylic acid derivatives and intermediates has received further attention from C. H. Fisher and co-workers. The preparation of methyl acetoxypionate from lactic acid and methyl acetate,<sup>38</sup> and from lactic acid, acetic acid, and methanol,<sup>39</sup> has been studied and reported on. The latter method appears to give the better yield and the relative costs of the methods are discussed. The most favourable conditions for the pyrolysis of methyl acetoxypionate to methyl acrylate have been found<sup>40</sup> to require reaction in stainless steel apparatus at temperatures about 500° at atmospheric pressure. A number of lactic esters of acrylic and methacrylic acids has also been examined.<sup>41</sup> The monomers were prepared by acetylating the lactic esters with acrylyl or methacrylyl chlorides or methacrylic anhydride and were polymerised in emulsion. Brittle points were measured and the properties of the polymers are discussed from the point of view of the cross-linking involved.

The preparation of  $\alpha$ -substituted acrylic acids from ketones by oxidation with hypochlorite solution has been claimed by the Röhm & Haas Co.<sup>42</sup> According to this claim methyl methacrylate in 50% yield is obtained from methyl  $\alpha$ -methylvinyl ketone. The same company has described<sup>43</sup> a process for preparing methacrylate esters from the corresponding esters of  $\alpha$ -hydroxyisobutyric acid.

The effects, on the polymerisation reaction and on the product, of the emulsifier and catalyst used have been investigated by W. C. Mast,

<sup>33</sup> U.S.P. 2,320,533; B., 1945, II, 150. U.S.P. 2,322,310; B., 1945, II, 225.

<sup>34</sup> *Chemurgic Digest*, 1945, 4, 85. *Lancet*, 1945, 248, 217.

<sup>35</sup> *Mod. Plastics*, 1945, 22, No. 10, 111.

<sup>36</sup> B.P. 569,974-5; B., 1945, II, 314. U.S.P. 2,310,132; B., 1944, II, 324.

<sup>37</sup> *Brit. Plastics*, 1945, 17, 30.

<sup>38</sup> C. E. Rehberg, W. A. Faucette, and C. H. Fisher, *Ind. Eng. Chem.*, 1944, 36, 469; B., 1944, II, 301.

<sup>39</sup> E. M. Filachione and C. H. Fisher, *ibid.*, 472; B., 1944, II, 301.

<sup>40</sup> W. P. Ratchford and C. H. Fisher, *ibid.*, 1945, 37, 382; B., 1945, II, 233.

<sup>41</sup> C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Amer. Chem. Soc.*, 1945, 67, 208; A., 1945, II, 208.

<sup>42</sup> U.S.P. 2,192,142; B., 1945, II, 259.

<sup>43</sup> U.S.P. 2,184,934; B., 1945, II, 45.



L. T. Smith, and C. H. Fisher.<sup>44</sup> The results have been discussed from the point of view of ease of control of the reaction and the stability of the emulsion, and several commercial emulsifiers are placed in order of preference for requirements such as an easily broken emulsion for the separation of the polymer and a stable emulsion for spraying and brushing.

The addition of a moulding lubricant, for example, aliphatic unsaturated acids such as stearic acid, to the mixture undergoing polymerisation has been described by E. I. Du Pont de Nemours & Co.<sup>45</sup> This company has also described<sup>46</sup> the polymerisation of alkyl methacrylates dispersed in water with small amounts of partially hydrolysed polyvinyl acetate. Röhm & Haas Co.<sup>47</sup> has claimed a process for the polymerisation of methacrylates, mixed with an ester of acrylic acid or with styrene, in which the monomeric mixture is injected through a small orifice into water at 90—125°; under these conditions polymerisation takes place in a few seconds, giving polymers suitable for moulding.

The vulcanisation of acrylic resins has been studied by C. H. Fisher and co-workers and reported in a series of papers. In the first of these<sup>48</sup> a report is given of the preparation of a number of saturated copolymers which were examined with regard to their vulcanisability. The authors have found that cyano, halogen, and phenoxy groups in the copolymer facilitate vulcanisation with such suitable agents as sulphur and quinone dioxime. The properties of several vulcanised copolymers have been tabulated. The second paper<sup>49</sup> deals with the preparation and properties of vulcanised or cross-link polymers. Copolymers of ethyl acrylate and small proportions of allyl maleate were prepared and the vulcanisation of the copolymer with various vulcanising agents and accelerators was studied. The properties of the vulcanised copolymers were examined and tabulated and the efficiencies of the various agents were assessed. Two of the conclusions reached are that ammonium persulphate is the preferred polymerisation catalyst and that cross-linked vulcanisates have greater hardness and tensile strength than those in which sulphur is used. In a third paper<sup>50</sup> a report has been given of the preparation of a series of unsaturated copolymers which were examined after being compounded with carbon black and vulcanised.

Among several copolymers described in the patent literature are a copolymer of vinyl acrylate and methacrylate with alkyl methacrylates and acrylates and the anhydrides of these acids which have been described by E. I. Du Pont de Nemours & Co.<sup>51</sup> as suitable for bonding abrasives,

<sup>44</sup> *Ind. Eng. Chem.*, 1945, **37**, 365; B., 1945, II, 247.

<sup>45</sup> U.S.P. 2,317,138; B., 1945, II, 118.

<sup>46</sup> U.S.P. 2,318,429; B., 1945, II, 165.

<sup>47</sup> U.S.P. 2,326,326; B., 1945, II, 312.

<sup>48</sup> W. C. Mast, C. E. Rehberg, T. J. Dietz, and C. H. Fisher, *Ind. Eng. Chem.*, 1944, **36**, 1022; B., 1945, II, 85.

<sup>49</sup> W. C. Mast, L. T. Smith, and C. H. Fisher, *ibid.*, 1027; B., 1945, II, 85.

<sup>50</sup> C. H. Fisher, W. C. Mast, C. E. Rehberg, and L. T. Smith, *ibid.*, 1032; B., 1945, II, 85.

<sup>51</sup> U.S.P. 2,321,728; B., 1945, II, 225.



and a granular copolymer of an ester of methacrylic acid and a vinyl-ethynylcarbinol which is suitable for moulding and which has been developed by Imperial Chemical Industries Ltd.<sup>52</sup>

### POLYSTYRENE.

No outstanding developments in the use of polystyrene have been reported in this year's literature, although a considerable amount of work has continued on polymers of halogenated styrenes and on copolymers. It may be expected that when the very considerable American capacity for styrene production is freed from the synthetic rubber programme, many new applications will be developed in that country in attempts to absorb the production. In this country, where polystyrene production is only just recovering from the recent war-time use of the plant for other products, the effect of the cheaper American production on the British plastics industry is still a subject for speculation.

Methods for the preparation of styrene have been described by the Carbide & Carbon Chemicals Corporation,<sup>53</sup> who pass ethylbenzene through a heated iron tube in the presence of a polyhalogeno-hydrocarbon, for example, carbon tetrachloride, and an aromatic base capable of forming a hydrohalide, *e.g.*, pyridine, and by G. Daumiller and G. Hoffmann,<sup>54</sup> who obtain a high yield by passing a carboxylic ester of  $\beta$ -phenylethyl alcohol through a copper-manganese tube. The Dow Chemical Co.<sup>55</sup> have claimed the use of substituted pyrocatechols as stabilisers for styrene.

C. Walling<sup>56</sup> has studied the polymerisation of styrene in phenolic solvents and has concluded that his results support a free radical, rather than a carbonium ion, mechanism for polymerisation under these conditions.

W. P. Hohenstein, S. Siggia, and H. Mark<sup>57</sup> have carried out experiments on the polymerisation of styrene in solution and in emulsion in water which were obtained by exposing water, in the latter case containing a soap, to styrene vapour. Potassium persulphate was used as a catalyst in the water. It was found that the presence of a soap lowered the activation energy of the system, and increased the rate of polymerisation and also the average degree of polymerisation. The inhibition period was shorter when the air or oxygen above the aqueous phase was replaced by nitrogen or a vacuum or when the temperature of the system was raised. The same authors<sup>58</sup> have also examined the polymerisation of styrene in agitated emulsion; from the results they have concluded that the length of the inhibition period increases with the average initial

<sup>52</sup> B.P. 566,202; B., 1945, II, 119.

<sup>53</sup> U.S.P. 2,189,771; B., 1945, II, 207.

<sup>54</sup> U.S.P. 2,310,762; B., 1944, II, 304.

<sup>55</sup> U.S.P. 2,181,102; B., 1944, II, 346.

<sup>56</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1602; A., 1945, I, 32.

<sup>57</sup> *India Rubber World*, 1944, **111**, 173; B., 1945, II, 84.

<sup>58</sup> *Ibid.*, 1945, **111**, 436; B., 1945, II, 186.



particle size and that the final polymer is rather inhomogeneous and contains a considerable proportion of short chains.

J. Abere, G. Goldfinger, H. Naidus, and H. Mark<sup>59</sup> have investigated the polymerisation of styrene catalysed by benzoyl peroxide in various solvents. The general conclusion is that the amount of polymer formed is proportional to the initial monomer and catalyst concentrations. The reaction curves for the polymerisation in methanol show irregularities due to polystyrene being insoluble in methanol and the formation of a gelatinous phase during the reaction. The data obtained have been used to calculate the initial number average degree of polymerisation.

A useful general review of the preparation, polymerisation, and properties of styrene and its polymers has been given by S. Booth.<sup>60</sup> The various methods of measuring molecular weight and molecular weight distribution are dealt with in some detail, and the effect of these factors on other properties is discussed.

Polymers of substituted styrenes, particularly nuclear-halogen-substituted styrenes, have received a fair amount of attention. J. C. Michalek and C. C. Clark<sup>61</sup> have examined the properties of six nuclear-substituted dichlorostyrenes. The polymerisation, in emulsion, of these monomers is more rapid and complete than that of styrene, and, with the exception of the 3:4 compound, all the polymers are soluble in aromatic hydrocarbons. Certain of the polymers have good heat-resistance, while copolymers with butadiene give interesting rubber-like products. The preparation of halogenated styrenes has also been reported by L. A. Brooks.<sup>62</sup> The three monochlorostyrenes have been prepared and examined by S. N. Uschakov and P. A. Matuzov.<sup>63</sup> These compounds polymerise and copolymerise more rapidly than styrene, and the products are said to possess greater mechanical strength and heat-resistance than polystyrene. These authors<sup>64</sup> have also examined the copolymerisation of *p*- and *o*-chlorostyrene with styrene and methyl methacrylate. Patents for these polymers have been taken out by the Mathieson Alkali Works for the preparation of dichlorostyrenes<sup>65</sup> and for rubber-like copolymers with conjugated dienes,<sup>66</sup> and by the Dow Chemical Co.<sup>67</sup> for interpolymers with esters and ethers having not less than two ethylenic linkings.

D. W. McCuaig and O. B. McIntire<sup>68</sup> have described the properties of an expanded form of polystyrene having a density of 1—2 lb. per cu. ft. The air cells in the foam are discrete and the material is stated to have

<sup>59</sup> *J. Physical Chem.*, 1945, **49**, 211; B., 1945, II, 309.

<sup>60</sup> *Brit. Plastics*, 1945, **17**, 130, 172, 200; B., 1945, II, 223.

<sup>61</sup> *Chem. Eng. News*, 1944, **22**, 1559; B., 1945, II, 84.

<sup>62</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 1295; A., 1944, II, 363.

<sup>63</sup> *J. Appl. Chem. Russ.*, 1944, **17**, 538; B., 1945, II, 310.

<sup>64</sup> *Ibid.*, 52; B., 1945, II, 222.

<sup>65</sup> B.P. 564,828; B., 1945, II, 7.

<sup>66</sup> B.P. 570,596; B., 1945, II, 313.

<sup>67</sup> U.S.P. 2,321,896; B., 1945, II, 225.

<sup>68</sup> *Mod. Plastics*, 1945, **22**, No. 7, 106; B., 1945, II, 381.



very good water-resistance and to retain its buoyancy after long periods of submersion.

### POLYVINYL CHLORIDE.

Compositions based on polyvinyl chloride have continued to be used as important substitutes for rubber and have now become firmly established in some fields which before the war were entirely dominated by rubber. It will be interesting to see, now that the war has ended and our rubber plantations are being recovered, whether polyvinyl chloride will be able to maintain its position in these fields. In this connexion, H. Barron, J. N. Dean, and T. R. Scott<sup>69</sup> have considered the relative merits of cable coverings of polyvinyl chloride and natural and synthetic rubber.

The use of polyvinyl chloride compositions for the preparation of prostheses<sup>70</sup> and as a soft lining for dentures<sup>71</sup> indicates an awakening interest of the medical and dental professions in these compositions. Similar compositions have continued to be developed for use in footwear, and several articles<sup>72</sup> have appeared describing the uses of vinyl resins in the boot and shoe industry. In the leather-cloth industry, also, polyvinyl chloride compositions are being used to an increasing extent on account of their excellent abrasion- and wear-resistance.

Several new processes for the preparation of vinyl halides have been described in the patent literature. The British Thomson-Houston Company<sup>73</sup> have passed purified acetylene, from generator gas obtained by the action of an electric arc on hydrocarbon oil, and hydrogen chloride over mercury and mercury chloride catalysts to get a high yield of vinyl chloride. The Distillers Company have described<sup>74</sup> a continuous process for obtaining vinyl chloride from a hot mixture of ethylene and ethylene dichloride by the action of chlorine in the presence of a catalyst. The same company have also described<sup>75</sup> the preparation of vinyl chloride by the passing of ethylene dichloride through hot aqueous caustic soda in the presence of certain ethers of glycol. E. I. Du Pont de Nemours & Co.<sup>76</sup> have claimed the use of halides of gold as catalysts for the preparation of vinyl halides from acetylene and hydrogen halides.

The use of certain resins containing amino-groups for the heat- and light-stabilisation of polyvinyl chloride has been described by E. I. Du Pont de Nemours & Co.<sup>77</sup> whilst the Wingfoot Corporation<sup>78</sup> have described the uses of alkali, alkaline-earth, and lead phthalimides or arylsulphonamides. The use of dioctyl sebacate as a plasticiser to impart low-

<sup>69</sup> *J. Inst. Elect. Eng.*, 1944, **91**, Part II, 297; B., 1944, II, 322.

<sup>70</sup> *Plastics (London)*, 1944, **8**, 573.

<sup>71</sup> *Brit. Dent. J.*, 1945, **78**, 140.

<sup>72</sup> *Brit. Plastics*, 1944, **16**, 541. *Mod. Plastics*, 1945, **22**, No. 11, 100.

<sup>73</sup> B.P. 566,003; B., 1945, II, 70.

<sup>74</sup> B.P. 568,569; B., 1945, II, 235.

<sup>75</sup> B.P. 569,291; B., 1945, II, 259.

<sup>76</sup> B.P. 570,848; B., 1945, II, 292.

<sup>77</sup> U.S.P. 2,190,776; B., 1945, II, 282.

<sup>78</sup> U.S.P. 2,319,953; B., 1945, II, 148.



temperature flexibility to polyvinyl chloride has been described<sup>79</sup> and compared with the dibutyl ester.

The Pritchett & Gold and E. P. S. Company<sup>80</sup> have described a process for the preparation of microporous plates for electric accumulators from polyvinyl chloride. The process involves preparing a dough comprising polyvinyl chloride, methylcyclohexanone, and a material, such as starch or dextrin, which can be removed subsequently to give the pores. The hot dough is extruded to the desired form and then heated to remove the solvent; the pores are then formed by removing the other component by a suitable means.

#### POLYVINYL ACETATE AND DERIVATIVES.

The literature for the period under review indicates no outstanding development in this field. Instead, the period seems to have been one of steady development of existing processes for the preparation and applications of these polymers.

New catalysts for the preparation of vinyl esters from acetylene have been described by the Carbide & Carbon Chemicals Corporation,<sup>81</sup> who use mercury derivatives of heteropoly-acids, *e.g.*, silicotungstic acid. This company<sup>82</sup> have also described the polymerisation of vinyl acetate in methyl acetate in a process in which the residual monomer and most of the solvents are removed after polymerisation, following which methyl alcohol is added and the remaining methyl acetate is removed by distillation to leave a solution of the polymer in methyl alcohol. Polymerisation inhibitors for vinyl esters have been described<sup>83</sup> by E. I. Du Pont de Nemours & Co., and include anhydrous ammonium salts of the lower aliphatic acids and certain metal resins.

The use of a small percentage of sebacic acid to prevent agglomeration of polymers of vinyl acetate during drying has been described by E. I. Du Pont de Nemours & Co.<sup>84</sup>

A process for the production of cast films from polyvinyl alcohol, involving the use of sodium dioctyl sulphosuccinate as a stripping agent, has been described by the same company.<sup>85</sup>

Aldehyde derivatives of polyvinyl alcohol appear to have received a considerable amount of attention. A process for preparing acetals from polyvinyl acetate has been described by the Eastman Kodak Co.,<sup>86</sup> in which the products from the solvent polymerisation of vinyl acetate are treated with hydrogen chloride under conditions that cause the polymer to hydrolyse partly and to react with the acetaldehyde formed from the de-esterification of the monomeric vinyl ester. Modified processes for

<sup>79</sup> *Rubber Age*, 1945, 56, 633; B., 1945, II, 222.

<sup>80</sup> B.P. 565,022; B., 1945, II, 29.

<sup>81</sup> U.S.P. 2,186,437; B., 1945, II, 131.

<sup>82</sup> U.S.P. 2,183,642; B., 1944, II, 368.

<sup>83</sup> B.P. 567,464 and 567,879; B., 1945, II, 165. U.S.P. 2,182,528; B., 1945, II, 27.

<sup>84</sup> B.P. 566,980; U.S.P. 2,317,149; B., 1945, II, 148.

<sup>85</sup> B.P. 566,144; B., 1945, II, 62.

<sup>86</sup> U.S.P. 2,326,048; B., 1945, II, 317.



the preparation of acetals from polyvinyl alcohol by reaction with the aldehyde in the presence of sulphuric acid have been described by E. I. Du Pont de Nemours & Co.<sup>87</sup> The Wingfoot Corporation<sup>88</sup> have described the use of salts of hexamethylenetetramine and of basic compounds such as guanidine and cyanamide.

Much attention appears to have been paid to plasticisers for acetals, as evidenced by the patent literature. Eastman Kodak Co.,<sup>89</sup> in a number of patents, have described the use of a very wide range of plasticisers for producing transparent rubbery sheets from polyvinyl acetals. Other plasticisers have been described by the Monsanto Chemical Co.<sup>90</sup> Other modifiers described in the patent literature include the use of aliphatic monohydroxy-carboxylic acids, *e.g.*, lactic or malic acid, to prevent acetals sticking to moulds, which is described by the Monsanto Chemical Co.,<sup>91</sup> and the heating of polyvinyl butyral with a lower alkyl ester of *p*-toluenesulphonic acid to reduce solubility and thermoplasticity, which is described by the Wingfoot Corporation.<sup>92</sup>

Among applications for the acetals, D. S. Plumb<sup>93</sup> has reviewed the use of plasticised polyvinyl butyral as an elastomer in the rubber industry, and S. N. Uschakov and co-workers<sup>94</sup> have reported on the use of several acetals for rendering concrete gasoline-proof.

Of the copolymers involving vinyl chloride most interest seems to have centred around vinyl chloride-vinyl acetate compositions, although the Wingfoot Corporation<sup>95</sup> have described the preparation of elastic products from plasticised copolymers of vinyl chloride-vinylidene chloride-vinyl acetate.

Heat-stabilisation of the chloride-acetate copolymer is effected, according to the Carbide & Carbon Chemicals Corporation,<sup>96</sup> by the addition of a mixture of certain metallic stearates with alkali metal acetates or formates. The dispersion of high molecular weight polymers and copolymers in a plasticiser to form a paste which is subsequently gelatinised, *e.g.*, on a shaped former, at about 170–220°, to form a thin film, has been described by Imperial Chemical Industries Ltd.<sup>97</sup>

The water- and grease-proofing of fibrous sheet material has been described by the Carbide & Carbon Chemicals Corporation,<sup>98</sup> who use for this purpose a plasticised vinyl halide-vinyl ester copolymer mixed

<sup>87</sup> B.P. 566,004 and 568,914; B., 1945, II, 120, 317.

<sup>88</sup> B.P. 567,130 and 569,383; B., 1945, II, 148, 294.

<sup>89</sup> U.S.P. 2,182,371 and 2,184,442–5; B., 1945, II, 29. U.S.P. 2,184,155; B., 1945, II, 44. U.S.P. 2,182,359–63; B., 1945, II, 62. U.S.P. 2,184,423 and 2,184,426; B., 1945, II, 87.

<sup>90</sup> U.S.P. 2,312,963; B., 1944, II, 328. U.S.P. 2,325,177; B., 1945, II, 281.

<sup>91</sup> U.S.P. 2,323,363; B., 1945, II, 280.

<sup>92</sup> B.P. 569,689; B., 1945, II, 312.

<sup>93</sup> *Ind. Eng. Chem.*, 1944, 36, 1035; B., 1945, II, 89.

<sup>94</sup> *J. Appl. Chem. Russ.*, 1944, 17, 125; B., 1945, II, 224.

<sup>95</sup> B.P. 563,720; B., 1944, II, 324.

<sup>96</sup> U.S.P. 2,181,478; B., 1944, II, 368.

<sup>97</sup> B.P. 566,388; B., 1945, II, 86.

<sup>98</sup> U.S.P. 2,185,356; B., 1945, II, 29.



with a compatible wax which is applied in the form of a film by means of heat and pressure in the absence of solvent.

### POLYAMIDES.

Although most of the literature and patents on polyamides deals with applications in the textile industries, an increased proportion of them this year deals with applications outside these industries, applications which indicate that polyamide compositions will enter most of the fields covered by other thermoplastics. Thus E. I. Du Pont de Nemours & Co. have described compositions for injection moulding,<sup>99</sup> extruded films,<sup>100</sup> wire coating,<sup>101</sup> artificial leather,<sup>102</sup> and for the production of transparent articles,<sup>103</sup> whilst A. G. Hovey<sup>104</sup> has discussed the use of polyamides from ethylenediamine and trimerised linoleic and linolenic acids as moisture vapour barriers, hot-dip coatings, lacquers, and wood-sealing compounds.

The use of a saturated solution of calcium chloride in methyl alcohol as a solvent for polyamides has been described by E. I. Du Pont de Nemours & Co.,<sup>105</sup> who state that a fine precipitate of the polyamide can be prepared from such a solution by the addition of a non-solvent, *e.g.*, methyl alcohol. The fine precipitate can then be used for the preparation of dispersions. The same company<sup>106</sup> have reported the use of hydroabietyl alcohol as a plasticiser for polyamides.

### POLYTHENE AND DERIVATIVES.

A considerable amount of literature on the history, production, and properties of polythene has again appeared this year. Several general reviews have appeared and new applications have been described. Among the latter, the production of ampoules from polythene has been described by Allen & Hanburys Ltd.<sup>107</sup> whilst Imperial Chemical Industries Ltd.<sup>108</sup> have described the use of polythene for making hollow articles, such as bottles and plugs. The British Nylon Spinners Ltd.<sup>109</sup> have used polythene for the production of threads and filaments, and E. I. Du Pont de Nemours & Co.<sup>110</sup> have described a process for the preparation of non-shrinking yarn from the polymer.

Several excellent papers have appeared giving detailed information on the properties of polythene. E. Hunter and W. G. Oakes<sup>111</sup> have

<sup>99</sup> U.S.P. 2,309,729; B., 1944, II, 325.

<sup>100</sup> B.P. 561,373; B., 1944, II, 325.

<sup>101</sup> U.S.P. 2,308,638; B., 1944, II, 329.

<sup>102</sup> U.S.P. 2,321,047; B., 1945, II, 189.

<sup>103</sup> B.P. 568,044; B., 1945, II, 225.

<sup>104</sup> *Mod. Plastics*, 1945, 22 No. 9, 125.

<sup>105</sup> B.P. 563,078; B., 1945, II, 71.

<sup>106</sup> U.S.P. 2,311,587; B., 1944, II, 366.

<sup>107</sup> B.P. 563,178; B., 1944, II, 334.

<sup>108</sup> B.P. 567,012; B., 1945, II, 147.

<sup>109</sup> B.P. 565,282; B., 1945, II, 78.

<sup>110</sup> U.S.P. 2,325,060; B., 1945, II, 268.

<sup>111</sup> *Brit. Plastics*, 1945, 17, 94; B., 1945, II, 223.



presented data on the thermal, physical, and chemical properties of the various grades of polythene produced. The electrical and most of the physical characteristics are identical for all the grades. The injection moulding, extrusion, and application of thick coats by hot dipping, of polythene are also described. The addition of polyisobutene to the polymer improves the flexibility at low temperatures but adversely affects the power factor and creep at high temperature. The same authors have investigated<sup>112</sup> the effect of temperature on the density of polythene and the relation between this effect and the crystallinity of the polymer. They have concluded that at room temperature solid polythene consists of about 55% of crystalline material, the remainder being amorphous. As the temperature is increased no change occurs up to 70°, after which the content of amorphous material increases at the expense of the crystalline, until the substance becomes wholly amorphous at 110—120°. The density of the molten polymer is considered to have little dependence on the molecular weight, but an increase in the molecular weight causes a rise in the temperature at which crystalline material first appears on cooling. Shock cooling causes the material to have a lower density than slow cooling, but annealing at 100° brings about a partial recovery of the abnormal density.

H. C. Raine, R. B. Richards, and H. Ryder<sup>113</sup> have investigated the relation between the degree of crystallinity of polythene and its specific heat and heat of dissolution. Heat contents were obtained and plotted against temperature, the curve showing a break at about 150°, corresponding to the melting point. The specific heat was obtained from the slope of this curve and plotted against temperature. By extrapolating the heat content-temperature curve for liquid polythene below the melting point it was possible to compare the heat content of the solid polythene with a hypothetical liquid polythene at any temperature. From this comparison the degree of crystallinity over a range of temperature was calculated, which agrees with the findings in the previous paper. R. B. Richards<sup>114</sup> has presented a mathematical interpretation of the relation between temperature and degree of crystallinity, and has considered the effect of the presence of low molecular weight material on the degree of crystallinity and on the depression of melting point.

R. B. Richards<sup>115</sup> has also reported on the remarkable chemical resistance of polythene. The polymer is not attacked at ordinary temperatures by strong oxidising agents, acids, and alkalis. Halogens are absorbed, but without much affect on the mechanical properties. Oxidation, which occurs in air above 120°, can be prevented by the incorporation of antioxidants. The resistance to organic solvents is excellent below

<sup>112</sup> *Trans. Faraday Soc.*, 1945, 41, 49; A., 1945, I, 162.

<sup>113</sup> *Ibid.*, 56; A., 1945, I, 162.

<sup>114</sup> *Ibid.*, 127; A., 1945, I, 162.

<sup>115</sup> *Brit. Plastics*, 1945, 17, 146; B., 1945, II, 223.



60°, but above this temperature the solubility of the polymers in hydrocarbons and halogenated hydrocarbons increases rapidly. Thus, in *m*-xylene at 130°, it is possible to get solutions of 50% polymer, and the author provides data on the viscosity of solutions of various grades of polythene at this temperature. The excellent chemical resistance of polythene renders it suitable for the protection of chemical plant, while the low moisture absorption and permeability render it a useful waterproof material in the film form.

Information on the oxidation of polythene and the effect on its properties has been presented by E. L. Midwinter,<sup>116</sup> who has described the most suitable conditions for processing polythene by moulding, extruding, casting, and other operations in order to avoid oxidation. The most important effects of oxidation are on the power factor and fluidity.

A comprehensive account of the properties of polythene, as compared with other plastics, has been given by F. C. Hahn, M. L. Macht, and D. A. Fletcher.<sup>117</sup>

#### OTHER POLYMERS.

A number of reviews have appeared describing the development, preparation, and properties of silicone resins. These are mainly of a general nature and detailed disclosures of the uses to which the silicone resins are being applied in America are still awaited. As yet there is no indication of the production of these resins in the United Kingdom.

Interesting developments in the handling of vinylidene chloride polymers include the addition of graphite to the polymer to increase the transverse strength of a filament obtained by cold drawing<sup>118</sup> and a process for fabrication in which the polymer is heated to its softening point and then rapidly chilled to give a supercooled material which is subjected to plastic deformation,<sup>119</sup> both of which have been described by the Dow Chemical Co.

Resinous copolymers of vinyl cyanide (acrylonitrile) and products of its partial hydrolysis and esterification, capable of giving elastic films, have been described by the Wingfoot Corporation.<sup>120</sup>

The polymerisation of diallyl esters of several acids to give infusible and insoluble products has been described by the American Cyanamid Co.,<sup>121</sup> and the Shell Development Co.<sup>122</sup> have described the preparation of polyallyl alcohol in which an ester of the alcohol is polymerised and then hydrolysed to give the polyalcohol; it is claimed that a polymer free from discoloration is obtained by this method. The preparation and polymerisation of a series of allyl ethers has been studied and reported

<sup>116</sup> *Brit. Plastics*, 1945, **17**, 208; B., 1945, II, 223.

<sup>117</sup> *Ind. Eng. Chem.*, 1945, **37**, 526; B., 1945, II, 309.

<sup>118</sup> U.S.P. 2,321,292; B., 1945, II, 188.

<sup>119</sup> U.S.P. 2,183,602; B., 1944, II, 366.

<sup>120</sup> B.P. 564,284; B., 1944, II, 368.

<sup>121</sup> U.S.P. 2,311,327; B., 1945, II, 119.

<sup>122</sup> B.P. 565,719; B., 1945, II, 70.



on by P. L. Nichols and E. Yanovsky<sup>123</sup>; they found that metal salts of organic acids accelerated polymerisation whereas alkalis appear to inhibit the reaction completely. The mechanism of the reaction is discussed on the basis of peroxide formation.

<sup>123</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 46; *A.*, 1945, **11**, 182.

## THERMOSETTING RESINS AND PLASTICS.

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A SURPRISING feature of the immediate post-war period has been the shortage of raw materials. As far as the phenolic plastics are concerned the reduction in output of coal has meant less coal tar and hence less phenol. It may well be that further expansion in phenolic plastics depends on the rehabilitation of the coal industry. There is an acute shortage of wood-flour since this is not coming from Sweden in the quantities required. The production of urea-formaldehyde moulding materials was more or less stopped during the war, urea resins being used as adhesives, a field in which they have been eminently satisfactory. Now that this demand has fallen off, urea-formaldehyde moulding materials are being made in greater quantity than before the war, but still the supply is insufficient. Moulders are also turning to cellulose acetate injection moulding materials for the production of many articles which would have been made in phenolic materials had they been available. It is possible that the present shortages of the well-established plastic materials may lead to a revival of the uses of and an improvement in the appearance of the despised "Muckite" materials—that is, moulding compositions made from inexpensive natural resins and fillers.

Cast phenolic resin, used before the war on account of its variety of colour and pattern as a decorative novelty material, is available again, but difficult to obtain. Likewise melamine-formaldehyde moulding materials are in production, but again difficult to obtain.

An interesting development in laminated materials now well established is that known as "post-forming"; in this process laminated cloth material bonded with a special phenolic resin is supplied in cured flat sheet form, such sheets being capable of a fair degree of hot-shaping by the employment of a simple technique.

## PHENOLIC PLASTICS.

### *Raw Materials.*

Chlorobenzene is converted into phenol by vaporisation with water at 350—650° over a catalyst such as calcium phosphate,<sup>1</sup> and the recovery

<sup>1</sup> Bakelite Corp., U.S.P. 2,311,777; *B.*, 1944, **11**, 305.



of phenols from petroleum washes by steam-distillation and further processing is described.<sup>2</sup> A method is given for the production of alkyl-phenols from halogenobenzenes condensed with an olefine or alkyl halide followed by hydrolysis.<sup>3</sup>

Formaldehyde is produced by the oxidation of methanol at 225—450° for 0.1—0.5 second in presence of a catalyst such as tungsten or molybdenum oxide in conjunction with promoters such as oxides of uranium, chromium, or iron.<sup>4</sup>

### *Phenolic Resin Production.*

No outstanding advances are apparent in phenolic resin production. Among the minor developments recorded are the use of chloroacetic acid in cast phenolic resins,<sup>5</sup> and the use of a colour-change indicator to show the extent of the mixing of a phenolic resin and acid hardener.<sup>6</sup> Variations described in the preparation of water-soluble phenolic resins include the use of a polyhydric alcohol during condensation,<sup>7</sup> the use of a high formaldehyde ratio,<sup>8</sup> and condensation in the presence of sulphur dioxide.<sup>9</sup>

Miscellaneous reaction products recorded include those made from phenol, formaldehyde, and dicyanodiamide<sup>10</sup>; phenol, formaldehyde, and an aliphatic ethenoid polymer<sup>11</sup>; phenol and cellulose<sup>12</sup>; phenol, formaldehyde, and a silicon derivative such as silicon tetrahalide<sup>13</sup>; phenol, formaldehyde, and urea<sup>14</sup>; phenol, formaldehyde, and pine wood pitch<sup>15</sup>; phenol and furfuryl alcohol<sup>16</sup>; and 1:12-bishydroxyphenyloctadecane and formaldehyde.<sup>17</sup>

A recent development in phenolic resin production has been the use of the long, unsaturated side-chain phenol, cardanol. A summary of the constitution, direct polymerisation, and condensation of cashew nutshell liquid, the active constituent of which is cardanol, is given.<sup>18</sup> Further details of the polymerisation reaction of cashew nutshell liquid with formaldehyde and furfuraldehyde are described.<sup>19</sup>

<sup>2</sup> Colgate-Palmolive-Peet Co., U.S.P. 2,324,467; B., 1945, II, 296.

<sup>3</sup> Dow Chemical Co., U.S.P. 2,193,760; B., 1945, II, 262.

<sup>4</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,320,253; B., 1945, II, 96.

<sup>5</sup> Amer. Cyanamid Co., U.S.P. 2,315,432; B., 1944, II, 368.

<sup>6</sup> Haveg Corp., U.S.P. 2,319,142; B., 1944, II, 368.

<sup>7</sup> Ford Motor Co., B.P. 565,472; B., 1945, II, 149.

<sup>8</sup> Bakelite Corp., U.S.P. 2,190,672; B., 1945, II, 282.

<sup>9</sup> Gen. Aniline & Film Corp., U.S.P. 2,321,451; B., 1945, II, 170.

<sup>10</sup> D. N. Vaskevitch and J. I. Baklashev, *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 354; B., 1945, II, 27.

<sup>11</sup> A. Wolfram and H. John, U.S.P. 2,322,990; B., 1945, II, 226.

<sup>12</sup> Chemical Foundation, U.S.P. 2,189,132—3; B., 1945, II, 192.

<sup>13</sup> Anderson-Stolz Corp., U.S.P. 2,182,208; B., 1945, II, 30.

<sup>14</sup> P. Cuvier, U.S.P. 2,315,087; B., 1944, II, 369.

<sup>15</sup> Hercules Powder Co., U.S.P. 2,324,758; B., 1945, II, 318.

<sup>16</sup> Gen. Aniline & Film Corp., U.S.P. 2,321,493; B., 1945, II, 191.

<sup>17</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,321,627; B., 1945, II, 226.

<sup>18</sup> J. D. Morgan, *J. Oil Col. Chem. Assoc.*, 1945, 28, 65; B., 1945, II, 247.

<sup>19</sup> Harvel Corporation, U.S.P. 2,323,131, 2,317,585, 2,317,587, 2,317,607, and 2,317,611; B., 1945, II, 317, 117. Custodis Construction Co., U.S.P. 2,317,116; B., 1945, II, 148.



*Phenolic Resin Compositions.*

The use of paper pulp-resin preforms for the production of large articles is receiving continued attention, and the methods of pulp preparation, resin addition, preform formation, and moulding production, together with a tabulated list of the properties of the mouldings, have been given.<sup>20</sup>

Moulding compositions are described as made from quebracho wood, formaldehyde, and a fibrous filler<sup>21</sup>; cresylic acid resin, wood flour, and flash or sweepings from previous operations<sup>22</sup>; phenolic resin and cottonseed hulls<sup>23</sup>; phenol, furfuraldehyde, and soya-bean meal<sup>24</sup>; and kapok and phenolic resin.<sup>25</sup> A moulding composition has been prepared by blowing powdered thermosetting phenolic resin into cotton lap.<sup>26</sup>

The infra-red preheating of moulding powders has been summarised,<sup>27</sup> and a method of obtaining variegated moulded effects by the use of a vibrating screen and stencils has been described.<sup>28</sup>

*Phenol-Formaldehyde Adhesives and Laminates.*

The production of phenolic adhesives has been described from soya-bean meal and a water-soluble phenolic resin<sup>29</sup>; a butadiene-acrylonitrile copolymer mixed with phenolic resin<sup>30</sup>; phenol, urea or thiourea, and formaldehyde mixed with cellulosic flour from pine, fir, and spruce<sup>31</sup>; partially polymerised phenol-formaldehyde resin dissolved in caustic soda<sup>32</sup>; and from a syrup of the cast resin type.<sup>33</sup>

A summary of the uses of synthetic resins in plywood manufacture has been given<sup>34</sup> and a method for calculating the time-temperature curing schedule.<sup>35</sup>

There has been some discussion on the properties desirable in paper used for the production of laminates,<sup>36</sup> and effects on the properties of

<sup>20</sup> R. H. Mosher, *Paper Mill News*, 1945, 68, 17; B., 1945, II, 267. R. H. Mosher, N. N. T. Samaras, and L. M. Debing, *Paper Trade J.*, 1945, 120, TAPPI Sect., 104; B., 1945, II, 222.

<sup>21</sup> Forestal Land Timber & Railways Co., Ltd., and E. H. W. Rottsieper, B.P. 567,495; B., 1945, II, 189.

<sup>22</sup> H. P. Bayon, B.P. 562,590; B., 1944, II, 326.

<sup>23</sup> Univ. of Tennessee Research Corp., U.S.P. 2,326,569; B., 1945, II, 315.

<sup>24</sup> J. A. Johnson, *Iowa State Coll. J. Sci.*, 1944, 19, 26; B., 1945, II, 276.

<sup>25</sup> P. Evans, and Kapok Ltd., B.P. 570,182; B., 1945, II, 320.

<sup>26</sup> Brit. Cotton Industry Res. Assoc., Bakelite Ltd., et al., B.P. 563,627; B., 1944, II, 324.

<sup>27</sup> T. A. Roberts and G. J. Happerfield, *Brit. Plastics*, 1945, 17, 302; B., 1945, II, 310.

<sup>28</sup> Hornflowa Ltd., and H. A. M. Winter, B.P. 566,837; B., 1945, II, 147.

<sup>29</sup> Ford Motor Co., B.P. 566,792; B., 1945, II, 120.

<sup>30</sup> B. B. Chemical Co., B.P. 569,666; B., 1945, II, 319.

<sup>31</sup> R. G. Peterson, U.S.P. 2,180,547; B., 1944, II, 371.

<sup>32</sup> I. F. Laucks, Inc., U.S.P. 2,186,369; B., 1945, II, 62.

<sup>33</sup> Catalin Corp. of America, U.S.P. 2,186,687; B., 1945, II, 62.

<sup>34</sup> T. D. Perry, *Brit. Plastics*, 1944, 16, 349, 465; B., 1944, II, 365.

<sup>35</sup> T. D. Perry, *Mod. Plastics*, 1944, 22, No. 2, 153; B., 1945, II, 277.

<sup>36</sup> L. V. Larsen, *Paper Trade J.*, 1945, 120, TAPPI Sect., 88; G. Alexander, *ibid.* 233; D. T. Jackson, *ibid.*, 257; B., 1945, II, 222, 267, 301.



the finished material by variation of the ingredients in the resin used and of methods for impregnating and laminating are described.<sup>37</sup> A method for low-pressure laminating<sup>38</sup> and the use of powdered phenolic resin with sheets primed with an aniline resin in the manufacture of laminated sheets are given.<sup>39</sup>

Punching grade material is stated to be obtained when a cardanol-modified phenol-formaldehyde resin is used.<sup>40</sup> Laminated materials which can be hot-shaped are obtained when the bonding resin is made from a fatty acid amide, protein, and phenolic resin.<sup>41</sup> A resin syrup of the cast phenolic type is described for laminating to give a product which is flexible and can be punched without fracture.<sup>42</sup>

The bonding of laminates by means of a high-frequency high-potential electric field is described and it is stated that the material can be made thermoplastic by the application of supersonic mechanical vibrations.<sup>43</sup>

A review has been given of recent manufacturing developments and the physical characteristics of paper-base laminates.<sup>44</sup> Further work on paper-base laminates has shown that by using densified paper of reduced void content, strong boards can be obtained with a pressure as low as 250 lb. per sq. in.<sup>45</sup>

## AMINO RESINS.

### *Raw Materials.*

The plant and method of production of thiourea from ammonium thiocyanate has been described.<sup>46</sup> Melamine is reported as being made by heating cyanamide or dicyanodiamide with liquid ammonia in methanol followed by pouring into water and treating with strong alkali<sup>47</sup>: melamine is purified, *e.g.*, freed from iron and other impurities, by treatment with water containing a hydroxy-compound, such as mannitol<sup>48</sup> or tartaric acid, which forms soluble iron compounds.

### *Urea-Formaldehyde Resins and Moulding Compositions.*

A comprehensive review on developments in urea- and melamine-formaldehyde resins for moulding powders, adhesives, etc. has been published.<sup>49</sup> A new method has been disclosed in which a syrup made from urea (1 mol.) and formaldehyde (1—2 mols.) is spray-dried to give

<sup>37</sup> H. Kline, *Paper Trade*, 1944, **119**, *TAPPI Sect.*, 128; B., 1945, II, 26.

<sup>38</sup> J. D. Nelson, *ibid.*, 1945, **120**, *TAPPI Sect.*, 3; B., 1945, II, 144.

<sup>39</sup> E. H. G. Sargent, B.P. 563,950; B., 1944, II, 369.

<sup>40</sup> Harvel Corp., U.S.P. 2,314,701; B., 1944, II, 367.

<sup>41</sup> E. H. G. Sargent, B.P. 567,128; B., 1945, II, 150.

<sup>42</sup> Catalin Corp. of America, U.S.P. 2,185,477; B., 1945, II, 30.

<sup>43</sup> Budd Wheel Co., B.P. 565,592; B., 1945, II, 120.

<sup>44</sup> T. A. Howells and H. F. Lewis, *Ind. Eng. Chem.*, 1945, **37**, 264; B., 1945, II, 177.

<sup>45</sup> K. W. Pepper and F. T. Barwell, *J.S.C.I.*, 1944, **63**, 321; B., 1945, II, 59.

<sup>46</sup> W. Klempt, *Chem. Technik*, 1942, **15**, 1; B., 1945, II, 161.

<sup>47</sup> Brit. Industrial Plastics, Ltd., B.P. 568,015; B., 1945, II, 208.

<sup>48</sup> Amer. Cyanamid Co., U.S.P. 2,324,450; B., 1945, II, 264.

<sup>49</sup> J. Hofton, *Chem. & Ind.*, 1944, 410; B., 1945, II, 60.



a product used in laminating and moulding powder production.<sup>50</sup> Cadmium stearate has been recommended as a lubricant for amino moulding compositions.<sup>51</sup>

The need for a really compatible plasticiser for amino resins is well known. Materials stated to be suitable for this purpose are monoethers of polyhydric alcohols, *e.g.*, monocresyl glyceryl ether,<sup>52</sup> the reaction product of polyamines with long-chain hydroxy-carboxylic acids,<sup>53</sup> certain high-molecular weight alcohols obtained by polymerising polyene acids or esters and hydrogenating the product,<sup>54</sup> and *N*-benzenesulphonylmorpholine.<sup>55</sup>

Interest is still maintained in accelerators for amino resin moulding compositions and the use of the following has been recorded: carbam-azide,<sup>56</sup> *O*-benzoyl-*NN*-dibenzylhydroxylamine,<sup>57</sup> oxanilic acid,<sup>58</sup> triethanolamine hydrochloride,<sup>58</sup> polysalicylide and complex nitriles,<sup>59</sup> the condensation product of a tertiary amine or alkylolamine and an acid,<sup>60</sup> halogenated ketones,<sup>61</sup> and ammonium sulphate and an alkaline-earth chloride.<sup>62</sup>

It has been proposed to modify urea-formaldehyde resins with bleached lac<sup>63</sup> and ethylene glycol.<sup>64</sup>

### *Melamine Resins.*

A completely water-miscible resin is stated to be obtained by interaction of methanol with polymethylolmelamine.<sup>65</sup> The use of melamine resins as ion-exchange products has been described.<sup>66</sup> Alkyl acetoacetates are claimed to be internal plasticisers<sup>67</sup> and halogenated acetamide acts as an accelerator for melamine resins.<sup>68</sup> Among the ingredients recorded as used in the production of modified melamine-formaldehyde resins are urea and thiourea,<sup>69</sup> protein and urea, thiourea, or dicyanodiamide,<sup>70</sup> and phenols.<sup>71</sup>

<sup>50</sup> Ellis-Foster Co., U.S.P. 2,192,129; B., 1945, II, 317.

<sup>51</sup> Plaskon Co., U.S.P. 2,193,670; B., 1945, II, 281.

<sup>52</sup> Brit. Industrial Plastics, Ltd., B.P. 567,705; B., 1945, II, 191.

<sup>53</sup> Amer. Cyanamid Co., U.S.P. 2,322,240; B., 1945, II, 226.

<sup>54</sup> *Idem*, U.S.P. 2,311,341; B., 1944, II, 368.

<sup>55</sup> Gen. Electric Co., U.S.P. 2,322,566—7; B., 1945, II, 225.

<sup>56</sup> Plaskon Co., U.S.P. 2,193,621; B., 1945, II, 281.

<sup>57</sup> *Idem*, U.S.P. 2,186,821; B., 1945, II, 62.

<sup>58</sup> Gen. Electric Co., U.S.P. 2,317,181; B., 1945, II, 119.

<sup>59</sup> *Idem*, U.S.P. 2,320,816—20; B., 1945, II, 189.

<sup>60</sup> Amer. Cyanamid Co., U.S.P. 2,326,727; B., 1945, II, 316.

<sup>61</sup> Gen. Electric Co., U.S.P. 2,323,898; B., 1945, II, 318.

<sup>62</sup> Plaskon Co., B.P. 564,762; B., 1945, II, 30.

<sup>63</sup> M. Sreenivasaya and P. S. Sarma, *J. Sci. Ind. Res., India*, 1944, 2, 227; B., 1944, II, 322.

<sup>64</sup> Reichhold Chemicals Inc., U.S.P. 2,185,167; B., 1945, II, 30.

<sup>65</sup> Amer. Cyanamid Co., B.P. 566,347; B., 1945, II, 87.

<sup>66</sup> *Idem*, B.P. 562,402—3, 566,789; B., 1944, II, 330; 1945, II, 121.

<sup>67</sup> Gen. Electric Co., U.S.P. 2,325,375—6; B., 1945, II, 313.

<sup>68</sup> *Idem*, U.S.P. 2,321,586; B., 1945, II, 226.

<sup>69</sup> *Idem*, U.S.P. 2,315,401; B., 1944, II, 370.

<sup>70</sup> *Idem*, U.S.P. 2,315,402; B., 1944, II, 370.

<sup>71</sup> *Idem*, U.S.P. 2,315,400; B., 1944, II, 369.



A number of complex triazines and pyrimidines have been patented as resin raw materials.<sup>72</sup>

### *Amino Resin Adhesives.*

A useful review of recent advances in the theory and methods of application of synthetic resin adhesives, particularly urea-formaldehyde resins, has been published.<sup>73</sup> Among the developments recorded in amino resin adhesives are the addition of phenylguanazole,<sup>74</sup> the use of foamed resin to reduce the amount of resin required,<sup>75</sup> ammonium chloride as a hardener in conjunction with ammonium borate as a retarder,<sup>76</sup> and methacrylic ester emulsions.<sup>77</sup> The use of urea- and melamine-formaldehyde adhesives in the production of paper laminates has been discussed.<sup>78</sup>

### *Analysis and Testing.*

A systematic scheme for the identification of synthetic resins and plastics has been prepared.<sup>79</sup> In the determination of phenols, the various methods reported include the use of infra-red absorption spectrometry,<sup>80</sup> galvanometric following of progressive bromination,<sup>81</sup> some refinements of the well-known Gibbs method,<sup>82</sup> and adaptations of the cloud point method.<sup>83</sup> Methods for the determination of formaldehyde<sup>84</sup> and furfuraldehyde are described.<sup>85</sup>

General methods have been developed for the identification of melamine and urea resins in papers of high wet strength.<sup>86</sup> There has been some discussion on the factors concerned in the determination of impact and shear strength,<sup>87</sup> bearing strength,<sup>88</sup> abrasion-resistance,<sup>89</sup> and water absorption<sup>90</sup> of plastic materials.

<sup>72</sup> Gen. Electric Co., U.S.P. 2,312,688—705; B.P. 564,999. Brit. Thomson-Houston Co., B.P. 564,576, 565,059, 569,413—5; B., 1944, II, 369; 1945, II, 318.

<sup>73</sup> N. A. de Bruyne, *Plastics*, 1945, 9, 228; B., 1945, II, 247.

<sup>74</sup> Aero Research, Ltd., B.P. 565,490; B., 1945, II, 120.

<sup>75</sup> A. Meuger and E. Bock, U.S.P. 2,323,831; B., 1945, II, 320.

<sup>76</sup> Plaskon Co., U.S.P. 2,193,630; B., 1945, II, 282.

<sup>77</sup> Röhm & Haas Co., U.S.P. 2,187,383; B., 1945, II, 87.

<sup>78</sup> C. H. Pottenger, *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 225; B., 1945, II, 267.

<sup>79</sup> T. P. G. Shaw, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 541; C., 1945, 29.

<sup>80</sup> H. W. Thompson and D. H. Whiffen, *Chem. & Ind.*, 1944, 343; C., 1944, 168.

<sup>81</sup> W. Bielenberg and K. Kühn, *Z. anal. Chem.*, 1943, 126, 88; C., 1944, 168.

<sup>82</sup> A. W. Beshgetoor, L. M. Greene, and V. A. Stenger, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 694; C., 1945, 21.

<sup>83</sup> J. Kay and P. J. C. Haywood, also W. Seaman, *ibid.*, 772; C., 1945, 104.

<sup>84</sup> G. C. Whitnack and R. W. Moshier, *ibid.*, 496; C., 1944, 166.

<sup>85</sup> K. T. H. Farrer, *J. Proc. Austral. Chem. Inst.*, 1944, 11, 186; C., 1945, 22. H. R. Rogers, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 319; C., 1944, 169.

<sup>86</sup> R. W. Stafford, W. M. Thomas, E. F. Williams, and N. T. Woodberry, *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 155; C., 1945, 170.

<sup>87</sup> D. R. Morey, *Ind. Eng. Chem.*, 1945, 37, 255; B., 1945, II, 187. P. M. Field, *Mod. Plastics*, 1944, 21, No. 8, 123; B., 1945, II, 276. R. J. Schwartz and E. Dugger, jun., *ibid.*, No. 7, 117; C., 1945, 219; B., 1945, II, 276. J. W. Maxwell, *Trans. Amer. Soc. Mech. Eng.*, 1945, 67, 104; B., 1945, II, 223.

<sup>88</sup> R. T. Schwartz and E. Dugger, jun., *Mod. Plastics*, 1944, 21, No. 9, 133; B., 1945, II, 277.

<sup>89</sup> E. R. Hoffman, *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 31; B., 1945, II, 187.

<sup>90</sup> J. Delmonte and L. Asselin, *Mod. Plastics*, 1944, 21, No. 9, 138. C., 1944, 203.



The effect of elevated temperature<sup>91</sup> and of low temperatures<sup>92</sup> on plastics has been discussed.

A most interesting paper has been published on the microscopical examination, including differential staining, of various reinforced plastic materials.<sup>93</sup> Naphthalene-formaldehyde resin is recommended as a mounting material for microscopic slides.<sup>94</sup>

There has been some speculation on the structure of melamine-formaldehyde<sup>95</sup> and furfuraldehyde resins<sup>96</sup> and on the hardening process of phenol-formaldehyde<sup>97</sup> resins, but very little light has been shed on the subject.

The Tyndall effect and low-angle X-ray diffraction have been used in the study of the structure of high polymers.<sup>98</sup>

<sup>91</sup> P. Norelli and W. H. Gard, *Ind. Eng. Chem.*, 1945, **37**, 580; B., 1945, II, 310.  
D. Baker and J. E. Gurvitch, *Mod. Plastics*, 1944, **22**, No. 1, 142; B., 1945, II, 277.

<sup>92</sup> W. Röhrs and K. H. Hauck, *India-Rubber J.*, 1945, **108**, 131; B., 1945, II, 116.

<sup>93</sup> C. M. Gordon, *J.S.C.I.*, 1944, **63**, 272; B., 1944, II, 322.

<sup>94</sup> W. D. Fleming, U.S.P. 2,312,329; B., 1944, II, 325.

<sup>95</sup> W. Feast, *Brit. Plastics*, 1945, **17**, 36, 66; B., 1945, II, 145.

<sup>96</sup> W. S. Penn, *ibid.*, 1944, **16**, 286; B., 1944, II, 363.

<sup>97</sup> E. Schauenstein and S. Bontempo, *Ber.*, 1943, **76**, [B], 75; B., 1945, II, 60.

<sup>98</sup> H. C. E. Johnson, *Chem. Industries*, 1945, **67**, 224; B., 1945, II, 187.

## CELLULOSIC PLASTICS.

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THE two most interesting features of the year have been the introduction of a new cellulosic plastic in the United States and the publication in this country of detailed reports on war-time developments in the German plastics industry. The commercial production of cellulose propionate plastic, announced late in the year,<sup>1</sup> has been made possible by the development of a method for producing propionic acid from natural gases. The new material appears to be intermediate in moulding properties between ethylcellulose and cellulose acetate butyrate, and to show excellent dimensional stability. A practical compromise has been achieved between the improved water-resistance and reduced rigidity which characterise plastics based on the higher fatty acid esters of cellulose. Whilst developments have so far been mainly in the field of moulding powders, the material is also expected ultimately to find application in the form of sheet and film, and large-scale production is planned for 1947.

In Germany the most impressive advances in plastics have unquestionably been those concerned with synthetic resins. Nevertheless technical teams which have investigated the production of cellulose derivatives

<sup>1</sup> R. H. Ball, *Mod. Plastics*, 1945, **23**, No. 4, 118. *Chem. Trade J.*, 1945, **117**, 500.



for plastics<sup>2</sup> and textiles<sup>3</sup> have reported some novel features in manufacturing processes, several of which are dealt with in the subsequent sections of this Report. Throughout the war wood pulp formed the sole available source of cellulose in Germany, the most successful variety being a nitric acid pulp<sup>4</sup> obtained from beechwood and having an  $\alpha$ -cellulose content of 98%. The successful war-time conversion to the use of wood pulp does not, however, appear to have lessened the universal preference for cotton linters as a raw material. For plastics manufacture the principal disadvantage arising from the employment of wood-cellulose derivatives was a reduced standard of colour and clarity in the finished product.

Substantial quantities of all the principal cellulosic plastics were being produced in Germany during the war. All phases of celluloid manufacture appear to have followed the established procedure. Cellulose acetate with 52—53% acetic acid content was being used in the manufacture of sheet and moulding powder and high-acetyl acetate was apparently used only in the preparation of safety film. Cellulose triacetate, acetate butyrate, and tripropionate were produced in somewhat smaller quantities and, in contrast to American developments, were being used mainly in the form of insulating foils. Applications of ethyl- and benzyl-cellulose, other than the water- and alkali-soluble grades, appear to have been confined to the formulation of insulating and water-resistant lacquers.

A German development<sup>5</sup> which merits attention, in view of the ever-increasing number of new products available, is the introduction of an informative code system for designating plastics in accordance with their chemical type and any special physical characteristics. It is reported<sup>6</sup> that a similar system is being instituted in the United States.

In this country as a result of the export drive the demand for both cellulose nitrate and acetate plastics in all forms has remained considerably in excess of actual production. Manufacturers have had to contend with the additional difficulty imposed by the competing flake requirements of the cellulose acetate rayon industry, this industry being itself the sole producer. Production of standard materials at full capacity throughout the war has hampered development work and this is evidenced by the fact that there are still no firm signs of the newer cellulosic products becoming available in important quantities. A temporary easing of the plasticiser situation following the relaxation of the control on phthalates in November has since been largely offset by the heavy consumption of higher phthalates in the manufacture of vinyl plastics. The continued absence of official figures for British plastics production is to be deplored. It is a pity that figures are not published which would do justice to the

<sup>2</sup> *B.I.O.S. Report, Item 22, Final Rept.* 185.

<sup>3</sup> *C.I.O.S. Report, Item 22, File XXVIII—1.*

<sup>4</sup> *Ibid.*, p. 108.

<sup>5</sup> *Elektrotech. Z.*, 1942, **63**, 267; 1943, **64**, 26; *Plastics*, 1945, **9**, 123.

<sup>6</sup> *Mod. Plastics*, 1945, **23**, No. 2, 134.



efforts and solid achievements of the industry during the war. United States sources again provide evidence of continued expansion in the cellulosic plastics section of the industry. Statistics released by the Department of Commerce<sup>7</sup> show that production of cellulosic plastics during 1944 amounted to approximately 81 million lb., while the figure for 1945 has been estimated<sup>8</sup> at 92 million lb. At the same time an even more significant growth is reported<sup>9</sup> in the production of vinyl plastics, the rigid forms of which are the principal competing group of materials, and in 1944 vinyls formed the major proportion of United States thermoplastics output for the first time.

#### CELLULOSIC RAW MATERIALS.

The cellulose raw material situation has been discussed by J. Grant,<sup>10</sup> who comments on the position of the paper and related industries as competitors for world cellulose supplies, and by N. Ahmad and M. G. Karnik,<sup>11</sup> who have studied the potentialities of a number of Indian cellulose-bearing materials, of which jute and hemp pulps were found to give the highest yields of  $\alpha$ -cellulose. A number of patents have dealt with improvements in the purification of wood and cotton cellulose although no radical changes are proposed. Patents of the Cellulose Research Corporation describe acid<sup>12</sup> and alkaline<sup>13</sup> digestion processes for wood pulp, giving a product with an  $\alpha$ -cellulose content of 98% and suitable for esterification. Details of the I.G. Farbenindustrie processes for sulphite and nitric acid wood pulp manufacture have now been disclosed.<sup>14</sup> Alkaline treatment at normal temperature preceding the usual digestion and bleaching processes is claimed by the Hercules Powder Co.<sup>15</sup> to yield cotton linters particularly suitable for conversion into plastics grade derivatives. A method for assessing the suitability for acetylation of purified wood pulp is described by G. Jayne and U. Schenck,<sup>16</sup> and depends on homogeneous acetylation under controlled conditions and comparison of the turbidity of the final reaction mixture before and after centrifugal removal of any undissolved residue.

Two interesting research investigations have been concerned with the development of a quantitative method, originally due to R. F. Nickerson,<sup>17</sup> for assessing the reactivity of cellulose. This method is based on the observation that while the hydrolysis and catalytic oxidation of cellulose

<sup>7</sup> *Mod. Plastics*, 1945, 23, No. 4, 134.

<sup>8</sup> *Chem. Met. Eng.*, 1946, 53, No. 1, 106.

<sup>9</sup> *Mod. Plastics*, 1945, 23, No. 4, 134.

<sup>10</sup> *Paper Maker*, 1944, 108, 7813; B., 1944, 11, 313.

<sup>11</sup> *J. Sci. Ind. Res. India*, 1944, 2, 275; B., 1944, 11, 352.

<sup>12</sup> L. M. Sheldon, L. E. Goff, M. L. Herzog, and F. Olsen, U.S.P. 2,185,776 and 2,187,710; B., 1945, 11, 16, 78.

<sup>13</sup> F. Olsen, U.S.P. 2,314,658; B., 1945, 11, 17.

<sup>14</sup> *C.I.O.S. Report, Item 22, File XXVIII-1*, p. 106.

<sup>15</sup> B.P. Appl. 14,796/45.

<sup>16</sup> *Cellulosechem.*, 1944, 22, 54; *Chem. Abs.*, 1945, 2402.

<sup>17</sup> *Ind. Eng. Chem. [Anal.]*, 1941, 13, 423; B., 1941, 11, 300.



by hydrochloric acid in presence of ferric chloride liberates carbon dioxide at an initially slow rate which increases as hydrolysis proceeds, the same reagent rapidly evolves carbon dioxide from glucose at an almost constant rate which is proportional to the amount of glucose present. R. F. Nickerson and J. A. Habrle<sup>18</sup> have suggested that the variation in the reaction rate is an effect of structural heterogeneity in the cellulose itself, and that anhydroglucose elements are less susceptible to hydrolysis in the highly ordered or crystalline regions than in transitional and disordered or amorphous regions. For the samples studied they have calculated that these components are present to the extent of 94, 3, and 3% respectively. In a study of the same reaction C. C. Conrad and A. G. Scroggie<sup>19</sup> have calculated "accessibility" values for different samples of cellulose, which represent the proportion of readily hydrolysed material, and have adduced evidence from X-ray measurements which suggests that these accessibility values are essentially a measure of the amorphous cellulose constituent.

#### MANUFACTURE AND PROPERTIES OF CELLULOSE DERIVATIVES.

Methods for pretreating cellulose to obtain increased reactivity have continued to engage attention. According to proposals of J. Fleischer and W. A. Bailey, jun.,<sup>20</sup> azeotropic distillation is employed in preparing water-wet wood pulp for esterification, the cellulose fibres being left free from water and swollen with a lower fatty acid. Processes of the Eastman Kodak Co. preface actual esterification by treating cellulose alternatively with a mixture of acetic and phosphoric acids,<sup>21</sup> with propionic acid containing a small proportion of sulphuric acid,<sup>22</sup> or successively with aqueous and anhydrous fatty acids.<sup>23</sup> Methods proposed for treating cellulose before nitration include mercerisation<sup>24</sup> and preliminary wetting with weak nitrating acid.<sup>25</sup> Saturation of the cellulose with a dilute solution of triethanolamine sulphate<sup>26</sup> is claimed to assist heterogeneous esterification, whilst F. C. Hahn<sup>27</sup> has found it advantageous in etherification to impregnate cellulose fibres with an alkali-stable wetting agent. A study of factors influencing the etherification process is also reported by S. N. Uschakov and N. V. Orlova,<sup>28</sup> who have described optimum conditions for the preparation of alkali-cellulose for ethylation and benzylation.

<sup>18</sup> *Ind. Eng. Chem.*, 1945, **37**, 1115; B., 1946, II, 116.

<sup>19</sup> *Ibid.*, 592; B., 1945, II, 300.

<sup>20</sup> Assrs. to Cellulose Research Corp., U.S.P. 2,191,525; B., 1945, II, 269.

<sup>21</sup> C. J. Malm and L. W. Blanchard, jun., U.S.P. 2,193,033; B., 1945, II, 269.

<sup>22</sup> C. J. Malm, U.S.P. 2,358,080.

<sup>23</sup> *Idem*, U.S.P. 2,315,973; B., 1945, II, 78.

<sup>24</sup> G. A. Richter, Assr. to Brown Co., U.S.P. 2,181,911; B., 1945, II, 18.

<sup>25</sup> R. H. McKee, U.S.P. 2,377,435.

<sup>26</sup> A. Marschall, and Deutsche Acetat-Kunstseiden A.-G., G.P. 715,929; *Chem. Abs.*, 1944, 2208.

<sup>27</sup> Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,190,450; B., 1945, II, 178.

<sup>28</sup> *J. Appl. Chem. Russ.*, 1944, **17**, 193; B., 1945, II, 266.



Publications dealing with the manufacture of the simple esters include a suggestion for the replacement of pyridine by dioxan in acetylisng cellulose with acetyl chloride in order to obtain a higher degree of substitution,<sup>29</sup> and a process of E. I. Du Pont de Nemours & Co. for the preparation of high-viscosity cellulose propionate.<sup>30</sup> The investigation of German processes for the manufacture of cellulose acetate has revealed a number of interesting technical developments and a rather surprising divergence of practice at different plants. In the process employed by the I.G. Farbenindustrie,<sup>31</sup> whose Dormagen plant showed a high degree of mechanisation and was considered to be the best examined, cellulose was pretreated with acetic acid and acetylated in 3500-kg. batches, using methylene chloride as diluent. In consequence of the small proportion of sulphuric acid catalyst necessary, acetylation and ripening were carried out at temperatures approaching 60°, and it was also found possible to dispense with the conventional stabilisation process; after precipitation the product was washed by a continuous countercurrent operation on a perforated conveyor belt, discharged through an automatically-ejecting centrifuge, and dried under vacuum.

High-temperature ripening processes in place of stabilisation form the subject of a series of patents granted to British Celanese Ltd., in which compounds of aluminium,<sup>32</sup> calcium, zinc, and magnesium<sup>33</sup> are employed for partial or complete neutralisation of the sulphuric acid catalyst, or in which the latter is replaced by an arylsulphonic acid.<sup>34</sup>

Among improvements which have been recorded in methods for stabilising cellulose esters are included treatment of precipitated cellulose acetate with steam under pressure,<sup>35</sup> and a process applicable to powder-precipitated cellulose acetate butyrate,<sup>36</sup> in which steam is blown into the wet mass after preliminary addition of an aqueous solution of the alkali-metal salt of a weak volatile acid. R. L. Stern<sup>37</sup> employs a specialised washing process for the stabilisation of fibrous cellulose nitrate, and E. Berl<sup>38</sup> has described the continuous nitration and stabilisation of cellulose tissue in which the catalyst is acetic anhydride or phosphorus pentoxide. An experimental study of cellulose nitrate stabilisation has been published by G. Centola,<sup>39</sup> who has investigated the effect of alcoholic extraction of nitrated cotton and concludes that

<sup>29</sup> P. V. Popov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **46**, 325; A., 1945, II, 226.

<sup>30</sup> R. E. Fothergill, U.S.P. 2,372,565.

<sup>31</sup> C.I.O.S. Report, Item 22, File XXVIII—1, p. 41.

<sup>32</sup> H. Dreyfus, B.P. 566,863; B., 1945, II, 138.

<sup>33</sup> B.P. 568,545; B., 1945, II, 240. B.P. 568,047, 568,051, and 568,098; B., 1945, II, 213.

<sup>34</sup> B.P. 567,893; B., 1945, II, 213.

<sup>35</sup> B. S. Farquhar and F. Schulze, Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,365,258.

<sup>36</sup> G. A. Kirton and J. B. Kemp, Assrs. to Eastman Kodak Co., U.S.P. 2,360,239.

<sup>37</sup> Assr. to Hercules Powder Co., U.S.P. 2,366,880.

<sup>38</sup> U.S.P. 2,384,415.

<sup>39</sup> *Annali Chim. Appl.*, 1941, **31**, 539; *Chem. Abs.*, 1945, 1539.



the resulting improvement in chemical stability is a function of the permeability of the intermicellar spaces.

The increasing importance of cellulose higher fatty acid and mixed esters and the predominantly American activity in this field are reflected in the relatively large number of patents dealing with improvements in preparative methods. Esterification is being carried out with mixed acid anhydrides. The Celanese Corporation of America employs formic acetic anhydride,<sup>40</sup> and I.G. Farbenindustrie acetic butyric anhydride,<sup>41</sup> in manufacturing the corresponding mixed esters. Variations in the type of catalyst used have been proposed to obtain higher fatty acid esters or mixed esters having high viscosity<sup>42</sup> and improved clarity.<sup>43</sup> Improved clarity is claimed by M. E. Martin and T. M. Andrews<sup>44</sup> to result when a solvent for the mixed ester is added to the ripening solution before precipitation. Mixed esters of dicarboxylic and lower fatty acids are prepared in the absence of a catalyst by heating the dicarboxylic acid anhydride and the fatty acid ester under pressure.<sup>45</sup>

Publications dealing with the manufacture of cellulose ethers and ether-esters have again been few in number. One development with interesting potentialities is the preparation of cellulose vinyl ether reported by A. E. Favorski and M. F. Schostakovski,<sup>46</sup> in which cellulose is heated with acetylene under pressure in presence of alkali. In preparing ethylcellulose according to processes of British Celanese Ltd., etherification is accomplished with ethyl sulphate in presence of alkali and tetraethylethylenediamine,<sup>47</sup> whilst a product with improved heat-stability is obtained by reprecipitation after dissolving in a polar solvent.<sup>48</sup> J. W. Fisher<sup>49</sup> obtains highly water-resistant derivatives by esterifying ethylcellulose with higher fatty acids in presence of metal halide catalysts.

The further reaction and cross-linking of partly substituted cellulose derivatives through the agency of bifunctional substances affords a means of improving resistance to heat and reducing sensitivity to the action of organic solvents, and a number of such treatments have again been described in the literature. Reagents suggested for the modification of cellulose nitrate include dicarbimides, derivatives of dimethylolurea, and *N*-substituted polyamides.<sup>50</sup> Typical of the many other miscellaneous

<sup>40</sup> G. W. Seymour and B. B. White, U.S.P. 2,363,091.

<sup>41</sup> *B.I.O.S., Item 22, Final Rept.* 185, p. 24.

<sup>42</sup> C. J. Malm and L. W. Blanchard, jun., Assrs. to Eastman Kodak Co., U.S.P. 2,379,310.

<sup>43</sup> I.G. Farbenindustrie A.-G., Belg.P. 448,146; *Chem. Abs.*, 1945, 1537.

<sup>44</sup> Assrs. to Celanese Corp. of America, U.S.P. 2,373,630.

<sup>45</sup> L. W. Blanchard, jun., and C. L. Crane, Assrs. to Eastman Kodak Co., U.S.P. 2,183,982; *B.*, 1944, II, 354.

<sup>46</sup> Russ.P. 59,308; *Chem. Abs.*, 1945, 947.

<sup>47</sup> H. Dreyfus, U.S.P. 2,381,972.

<sup>48</sup> B.P. Appl. 8590/45.

<sup>49</sup> British Celanese Ltd., B.P. 571,572; *B.*, 1945, II, 373.

<sup>50</sup> R. J. W. Reynolds, E. E. Walker, and Imperial Chemical Industries Ltd., B.P. 567,940; *B.*, 1945, II, 178.



proposals for this purpose are the use of substituted polymethylene-diamides,<sup>51</sup> substituted diarylamines,<sup>52</sup> and esterification with certain dibasic acids.<sup>53</sup> The more important publications dealing with the properties of cellulose derivatives have been concerned with different aspects of polymolecularity and W. Badgley, V. J. Friette, and H. Mark<sup>54</sup> have given a general survey of recent progress in this field. Two further contributions from the laboratories of the U.S. National Bureau of Standards revise some details of earlier work<sup>55</sup> on the relationship between mechanical properties and degree of polymerisation in fractionated cellulose acetate. The number-average degree of polymerisation has been determined osmotically for fifteen different fractions obtained from a sample of commercial cellulose acetate.<sup>56</sup> The values obtained have been correlated<sup>57</sup> satisfactorily with the mechanical properties of films prepared from the different fractions. Simple blends of these fractions are found to have properties which approximate to the weight-average value for the separate components. Fractional dissolution of cellulose acetate has been employed by F. Howlett and A. R. Urquhart<sup>58</sup> in studying the distribution of chain length; a review and useful bibliography of fractionation methods is given in this paper. The properties of cellulose derivatives in solution are the subject of papers by A. Tager and V.A. Kargin,<sup>59</sup> who have measured the heats of solution of cellulose nitrate and acetate in a number of different solvents, and J. J. Hermans,<sup>60</sup> who investigated the viscosity of a number of polymers, including cellulose nitrate and triacetate, in dilute solution; Hermans has advanced a theory of the viscosity of dilute solutions according to which the dissolved polymer molecules are considered as flexible coils which undergo distortion in falling through the streaming field and have a finite relaxation time in which they revert to their original shapes. A new viscosity-molecular weight relation for cellulose acetate in acetone, applicable over a wider range of molecular weights than the equations of Staudinger and Mark, has been proposed by W. J. Badgley.<sup>61</sup> H. Mark<sup>62</sup> has discussed the chemical and physical changes in high-molecular weight polymers produced by ultrasonic vibrations. In the higher-frequency range the absorption of energy is sufficient to produce depolymerisation and irreversible decrease in the viscosity of cellulose nitrate solutions, whilst at lower frequencies

<sup>51</sup> S. Peterson and P. Schlack, U.S.P. 2,320,704; B., 1945, II, 178.

<sup>52</sup> S. L. Bass, L. A. Rauner, and P. H. Lipke, Assrs. to Dow Chemical Co., U.S.P. 2,383,361.

<sup>53</sup> American Viscose Corp., B.P. Appl. 1684/45.

<sup>54</sup> *Ind. Eng. Chem.*, 1945, 37, 227; B., 1945, II, 210.

<sup>55</sup> A. M. Sookne and M. Harris, *J. Res. Nat. Bur. Stand.*, 1943, 30, 1; B., 1944, II, 310.

<sup>56</sup> *Ibid.*, 1945, 34, 459; B., 1945, II, 300.

<sup>57</sup> *Ibid.*, 467; B., 1945, II, 300.

<sup>58</sup> *Shirley Inst. Mem.*, 1945, 19, 79; *J. Text. Inst.*, 1946, 37, T89; B., 1946, II, 371.

<sup>59</sup> *J. Phys. Chem. Russ.*, 1941, 15, 1036; A., 1943, I, 152.

<sup>60</sup> *Kolloid-Z.*, 1944, 106, 22; A., 1945, I, 26.

<sup>61</sup> *Polymer Bull.*, 1945, 1, 17.

<sup>62</sup> *J. Acoust. Soc. Amer.*, 1945, 16, 183.



only intermolecular bonds are ruptured and temporary decreases in viscosity may be subsequently restored by Brownian movement.

### PLASTICISERS AND SOLVENTS.

Substitute plasticisers were used fairly successfully during the period of phthalate shortage, which proved less serious in the event than had been anticipated. Glyceryl esters were the principal alternative plasticisers in this country, and in America these were supplemented by the use of citrates and 2-nitrodiphenyl. United States developments continue to dominate this field and the most significant recent advance has been the commercial production of resinous polymeric plasticisers. These materials excel in a number of qualities such as permanence, non-migration, and general resistance, although a somewhat lower plasticising efficiency necessitates their use in higher proportions than monomeric types. K. K. Fligor and J. K. Sumner<sup>63</sup> found that a sebacic acid polyester varied considerably in its compatibility with different cellulose derivatives. Modification of the starting materials to produce other polyesters for specific purposes is an indicated development, and a patent filed by C. Opp<sup>64</sup> describes a polymer which is suitable for plasticising cellulose acetate and acetate propionate. Acetals of hydroxycarboxylic acids described by E. I. Du Pont de Nemours & Co.<sup>65</sup> form resins with polyhydric alcohols and are said to be solvents and plasticisers for a wide range of cellulose derivatives. The literature contains many other miscellaneous proposals for new plasticisers. Among those suggested as being generally applicable with cellulose esters are ester-lactones<sup>66</sup> prepared by hydrogenation of  $\beta$ -(2-furyl)acrylic acid, phosphoric esters of nitro-alcohols,<sup>67</sup> substituted arylsulphonocyclohexylamides,<sup>68</sup> and bis(alkyl carbonates) of diethylene glycol.<sup>69</sup> The Hercules Powder Co.<sup>70</sup> claims the use of *p*-tert.-alkylphenoxyethanols as extenders in plasticising high-acetyl cellulose acetate. Acid- and alkali-resistant ethylcellulose compositions make use of ether-type plasticisers such as hydroxyalkyl ethers of benzophenone,<sup>71</sup> cyclohexylphenyl ethers and halogenated diphenyl ethers,<sup>72</sup> whilst hydroxy- or acyloxy-stearic acid<sup>73</sup> is employed in formulating low-temperature impact-resistant materials. Limited

<sup>63</sup> *Ind. Eng. Chem.*, 1945, **37**, 504; B., 1945, II, 277.

<sup>64</sup> Assrs. to Internat. Chem. Co., U.S.P. 2,385,377.

<sup>65</sup> D. J. Loder, W. F. Gresham, and D. B. Killian, U.S.P. 2,364,455.

<sup>66</sup> R. Leonard and J. J. Gordon, Assrs. to Eastman Kodak Co., U.S.P. 2,364,358.

<sup>67</sup> B. M. Vanderbilt, Assr. to Commercial Solvents Corp., U.S.P. 2,177,757; B., 1945, II, 44.

<sup>68</sup> L. P. Kyrides, Assr. to Monsanto Chem. Co., U.S.P. 2,180,281; B., 1944, II, 354.

<sup>69</sup> I. E. Muskat and F. Strain, Assrs. to Pittsburgh Plate Glass Co., U.S.P. 2,381,511.

<sup>70</sup> U.S.P. 2,379,036.

<sup>71</sup> G. H. Coleman and C. L. Moyle, Assrs. to Dow Chem. Co., U.S.P. 2,182,786; B., 1945, II, 52.

<sup>72</sup> Dow Chem. Co., U.S.P. 2,189,337—8; B., 1945, II, 190.

<sup>73</sup> M. J. Hunter and E. L. Kropscott, Assrs. to Dow Chem. Co., U.S.P. 2,385,359.



quantities of an important new class of solvents, the nitroparaffins,<sup>74</sup> are being made available in this country. Nitropropanes develop a strong solvent action for cellulose acetate in presence of alcohols, forming solutions which have a high tolerance for hydrocarbon diluents. In combination with alcohols and hydrocarbons they can also largely replace the toxic chlorinated cellulose triacetate solvents.

The thermodynamical basis of polymer-plasticiser interaction has been discussed by E. M. Frith and R. F. Tuckett,<sup>75</sup> who point out that it is unnecessary to assume complex-formation in order to explain the process of dissolution. The determining factor is considered to be the influence of the entropy of mixing in producing a change of free energy which favours dissolution. Assessment of the compatibility of polymers with plasticisers and solvents then involves measurement of the heats and entropies of mixing. In an experimental approach to the problem E. M. Frith<sup>76</sup> has measured the relative compatibility of plasticisers using viscosity-concentration curves for dilute solutions of polymers in mixed solvents containing plasticiser. In this connexion H. M. Spurlin<sup>77</sup> has drawn attention to some factors which must be considered in attempting to relate such viscosity measurements with solvent power.

A useful survey of recent trends in the utilisation of plasticisers and solvents has been given by W. E. Cash.<sup>78</sup>

#### MANUFACTURE AND MANIPULATION OF CELLULOSIC PLASTICS.

Although the raw material position renders parallel trends here improbable, the progress of cellulosic plastics has entered an interesting phase in the United States, where an ordered pattern of development is now beginning to emerge from the highly competitive situation of the last few years. American production of cellulose nitrate plastics is generally considered to have reached a peak value during 1945 and celluloid manufacturers are expecting a gradual decline in home consumption of the material. Active legislation against the use of inflammable plastics, and the variety of alternative materials available, are the principal factors contributing to this view. Cellulose acetate plastics have now attained major importance. Progress has been made notably in two main directions, the production of transparent packaging sheet in continuous rolls by solvent-less extrusion and the general introduction of moulding powder based on the use of flake of high acetyl content, which now forms the principal general-purpose injection-moulding material. Cellulose acetate butyrate is being absorbed in specialised applications such as the extrusion of sections and the production of injection mouldings where the over-riding importance of dimensional

<sup>74</sup> Anon., *Ind. Chem.*, 1944, 20, 144.

<sup>75</sup> *Nature*, 1945, 155, 164.

<sup>76</sup> *Trans. Faraday Soc.*, 1945, 41, 90; A., 1945, I, 163.

<sup>77</sup> *Polymer Bull.*, 1945, 1, 74.

<sup>78</sup> *Chem. Age*, 1945, 52, 77.



stability warrants the use of a higher-cost material. Other current developments with cellulose acetate butyrate are the production of gel-lacquer and hot-melt coating compositions and foil for cable insulation. In the same way, ethylcellulose also appears to be developing in directions which utilise its special qualities of strength and low-temperature resistance rather than as a general-purpose material. Ethylcellulose is also finding extensive use in the form of hot-casting and hot-dipping compositions. Preliminary reports of cellulose propionate augur well, but the material has yet to stand up to the searching tests of large-scale use and find its level in straight competition with the other cellulosic plastics. In the United States present indications are that no one of these materials will displace the others, but that in the foreseeable future the different materials will co-exist, each with particular spheres of usefulness.

The literature available for review in this section is virtually confined this year to material which has appeared in patents. A process study which is of interest, in view of the essential similarity between the manufacture of cordite and celluloid, is a paper by A. Soler<sup>79</sup> on the gelatinisation of cellulose nitrate by nitroglycerin. From acetylation and viscosity measurements on samples of the colloid taken during the rolling process the author has obtained confirmatory evidence that unesterified hydroxyl groups in the cellulose nitrate become involved in complex formation.

No outstanding developments have been recorded in connexion with the conventional block process for manufacturing material in sheet form, but the Plax Corporation<sup>80</sup> and the Dow Chemical Co.<sup>81</sup> describe improvements in the production of continuously extruded sheet.

Several patents of interest have appeared in connexion with the manufacture of films. Improvements in casting technique have been described in a series of patents filed by the Eastman Kodak Co.,<sup>82</sup> according to which increased casting speeds have been obtained through the use of gelable casting solutions in which the solvent-balance is so adjusted that they are liquid at temperatures above 50° and form clear, transparent, self-supporting gels when cooled. The hot solution is cast on a cold support and the film can be removed while still retaining up to 50% of solvent. Other improvements disclosed include the incorporation in the casting solution of high-molecular weight polyglycol esters of dicarboxylic acids as release agents to assist removal of the solvent-laden film from the casting surface,<sup>83</sup> and the employment of 2-amylcyclohexyl phosphate<sup>84</sup> and alkyl sulphates and alkylarylsulphonates<sup>85</sup> in

<sup>79</sup> A. Soler, *Ion*, 1944, 4, 455; *Chem. Abs.*, 1945, 1055.

<sup>80</sup> J. Bailey, U.S.P. 2,365,326.

<sup>81</sup> J. J. Grebe and E. H. Harder, U.S.P. 2,361,369.

<sup>82</sup> U.S.P. 2,319,051—5; B., 1945, II, 138. U.S.P. 2,367,503.

<sup>83</sup> H. L. Bolton and A. B. Savage, Assrs. to Dow Chem. Co., U.S.P. 2,388,206.

<sup>84</sup> J. B. Dickey, Assr. to Eastman Kodak Co., U.S.P. 2,318,296; B., 1945, II, 178.

<sup>85</sup> E. Schweizer, Assr. to Celanese Corp. of America, U.S.P. 2,365,297.



reducing the tendency for films to accumulate a static charge. In this connexion there is an interesting observation by J. K. Speicher<sup>86</sup> that films of ethylcellulose containing approximately 20% of cellulose nitrate have virtually no tendency to become charged. Improvements in some details of film-casting equipment have also been described.<sup>87,88</sup>

The manufacture of moulding powders has been mainly investigated with a view to increasing the resistance of materials to discoloration at high temperature. This problem has lately become a matter of urgent importance with the use of harder formulations as a means to achieving greater dimensional stability in finished mouldings. The influence of ultra-violet light in promoting the degradation of cellulosic materials is well-known, and a number of methods have been proposed for reducing the permeability of materials to this type of radiation. New stabilisers proposed specifically for use with ethylcellulose include menthylphenol<sup>89</sup> and derivatives of quinol<sup>90</sup> and pyrocatechol.<sup>91</sup> Stabilising additions to prevent high-temperature discoloration of cellulose mixed ester compositions include alcohol amines<sup>92</sup> and certain acids.<sup>93</sup> Proposals for reducing the permeability of cellulosic materials to ultra-violet irradiation include the addition of small quantities of acid quinine salts,<sup>94</sup> alkyl-benzylideneacetophenones,<sup>95</sup> alkyl- and aryl-fluoranthenes,<sup>96</sup> and esters of aromatic monocarboxylic acids.<sup>97</sup>

Recent developments in the formulation of cellulose derivative compositions for specialised applications include cellulose acetate butyrate gelable lacquers<sup>98</sup> which are fluid when hot and set on cooling while still containing residual solvent, and hot-melt coating compositions<sup>99</sup> prepared from the same derivative. An interesting development involving ethylcellulose is the preparation of an elastomer<sup>100</sup> by interaction of ethylcellulose with a polyphenyl hydrocarbon and a hydrogenated higher fatty acid glyceride. Specially formulated cellulose acetate moulding compositions have been developed with improved flame-resistance.<sup>101</sup>

Patents dealing with extrusion are again mainly concerned with machine design, and those of interest include details of methods for

<sup>86</sup> Assr. to Hercules Powder Co., U.S.P. 2,324,887; B., 1945, II, 270.

<sup>87</sup> G. F. Nadeau, Assr. to Eastman Kodak Co., U.S.P. 2,369,484.

<sup>88</sup> C. E. Coleman, Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,387,718.

<sup>89</sup> Anon., *Pacific Plastics*, 1945, 3, No. 8, 44.

<sup>90</sup> J. S. Tinsley, Assr. to Hercules Powder Co., U.S.P. 2,375,708.

<sup>91</sup> W. W. Koch, Assr. to Hercules Powder Co., U.S.P. 2,389,370.

<sup>92</sup> C. J. Malm and M. Salo, Assrs. to Eastman Kodak Co., U.S.P. 2,371,768.

<sup>93</sup> R. L. Stern, Assr. to Hercules Powder Co., U.S.P. 2,365,652.

<sup>94</sup> D. H. Jacobs, Assr. to Celanese Corp. of America, U.S.P. 2,370,244.

<sup>95</sup> W. Horback, Assr. to Celanese Corp. of America, U.S.P. 2,356,849.

<sup>96</sup> British Celanese Ltd., B.P. 569,920; B., 1945, II, 304.

<sup>97</sup> H. Dreyfus, B.P. 563,287; B., 1944, II, 315.

<sup>98</sup> M. Salo and H. F. Vivian, Assrs. to Eastman Kodak Co., U.S.P. 2,387,773.

<sup>99</sup> Idem, U.S.P. 2,387,774.

<sup>100</sup> H. Keller, Assr. to Monsanto Chem. Co., U.S.P. 2,388,613.

<sup>101</sup> M. Bentivoglio and B. E. Cash, *Mod. Plastics*, 1945, 22, No. 10, 102; B., 1946, II, 211.



measuring extrusion pressure<sup>102</sup> and controlling the size of tubes after extrusion.<sup>103</sup>

One of the most attractive possibilities in injection-moulding lies in the successful application of radio-frequency preheating methods for softening material immediately before injection. An account of progress in methods of cylinder-heating has been given by I. Thomas.<sup>104</sup> Whilst by far the greater part of injection-moulding work is still carried out in machines with rated capacities of 8 oz. or under, multi-cylinder machines have been produced with capacities as high as 36 oz., and a more detailed description has now been given of the combination extrusion-injection machine developed by the Chrysler Corporation<sup>105</sup> which is capable of producing 8-lb. mouldings.

One effect of the war was to give impetus to the study of methods for producing light-weight expanded cellular products, and developments in this field provide the most interesting feature of recent progress in manipulative technique. Typical methods have been described in a series of patents granted to British Celanese Ltd. In one process the cellulose derivative is first formed into a gel in a mixture of a solvent and a non-solvent and a cellular structure is produced by differential extraction or evaporation of the solvent mixture.<sup>106</sup> Alternative processes for the preparation of low-density products involve subjecting a solvent-impregnated cellulose derivative to high temperature and pressure and causing expansion to take place by releasing the pressure; coarse particles of the expanded material are then impregnated with a polymerisable synthetic resin and united by curing under light pressure.<sup>107</sup> Products with improved high-temperature resistance are obtained if the thermoplasticity of the expanded particles is destroyed by saponification before impregnation with the binding agent.<sup>108</sup> Physical data on experimentally developed extruded cellular cellulose acetate produced in America have been quoted by C. C. Sachs.<sup>109</sup>

Miscellaneous improvements in methods for forming three-dimensional shapes by blowing<sup>110</sup> and the combined use of infra-red heating and vacuum-forming<sup>111</sup> have also been described.

#### PHYSICAL PROPERTIES AND TESTING OF CELLULOSIC PLASTICS.

Published research investigations in this section have with few exceptions been contributed by American laboratories. Following the trend

<sup>102</sup> R. T. Fields, Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,369,553.

<sup>103</sup> C. E. Slaughter, Assr. to Extruded Plastics Inc., U.S.P. 2,383,520.

<sup>104</sup> *Mod. Plastics*, 1945, 23, No. 2, 135.

<sup>105</sup> N. J. Rakas and W. B. Cousino, *ibid.*, No. 4, 133.

<sup>106</sup> J. G. Williams, B.P. 565,343; B., 1945, II, 137.

<sup>107</sup> British Celanese Ltd., B.P. 568,535; B., 1945, II, 248.

<sup>108</sup> *Idem*, B.P. 568,543; B., 1945, II, 248.

<sup>109</sup> *Mod. Plastics*, 1945, 23, No. 4, 173.

<sup>110</sup> Dixon Plastics Ltd., B.P. 568,090.

<sup>111</sup> E. I. Du Pont de Nemours & Co., B.P. 569,813; B., 1945, II, 284.



of recent years, much of the work is of an essentially practical nature and deals with the evaluation of materials under conditions which may be encountered in normal usage. A comprehensive study of the effect of environmental conditions on the permanence of cellulose acetate and nitrate sheet materials is reported by T. S. Lawton, jun., and H. K. Nason.<sup>112</sup> Deterioration of these materials by weathering and exposure to heat, ultra-violet light, and moisture has been given quantitative expression in terms of changes in mechanical and optical properties and the molecular weight of the basic cellulose derivatives. The same authors have also investigated the degradation of thin films of cellulose acetate and nitrate by ultra-violet light in different atmospheres and find that degradation, as indicated by decrease in intrinsic viscosity, takes place more slowly in nitrogen than in either air or oxygen.<sup>113</sup> A further paper by these authors, in collaboration with T. S. Carswell,<sup>114</sup> deals with the effect on mechanical properties of variations in relative humidity and ambient temperature and some other details of test procedure. Factors influencing the ageing characteristics of plasticised cellulose acetate films have also been studied by Russian workers,<sup>115</sup> who observed that the degradative action of outdoor exposure was less pronounced with samples of high initial viscosity, but was accentuated by the omission of plasticiser or by the use of impure acetone in preparing the samples. Interesting data have been reported by W. E. Gloor<sup>116</sup> on the relative dimensional stability under extreme conditions of injection-moulded test specimens prepared from several grades of high-acetyl acetate, cellulose acetate butyrate, and ethylcellulose; for equivalent degrees of shape retention harder flow grades were necessary when using the acetate and acetate butyrate materials. Factors affecting the dimensional stability of cellulosic plastics have also been discussed by R. Burns.<sup>117</sup>

In a further paper on the measurement of creep, W. N. Findley<sup>118</sup> has successfully expressed creep data for a number of materials as a power function of time, and the results obtained indicate the possibility of extrapolating observed data to predict creep behaviour over much longer periods than those studied. Deficiencies inherent in existing methods of impact-testing have been discussed both by D. Telfair and H. K. Nason,<sup>119</sup> who have drawn attention to the importance of the state of stress produced in the specimen during the test and of dimensional changes which induce brittle-ductile transition phenomena, and by

<sup>112</sup> *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 259; *Mod. Plastics*, 1945, **22**, No. 5, 145; B., 1945, II, 347.

<sup>113</sup> *Ind. Eng. Chem.*, 1944, **36**, 1128; B., 1945, II, 77.

<sup>114</sup> *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 23.

<sup>115</sup> V. A. Karfunkel and D. A. Federov, *J. Appl. Chem. Russ.*, 1940, **13**, 1375; V. A. Karfunkel, *ibid.*, 1384; B., 1945, II, 13.

<sup>116</sup> *Product Eng.*, 1945, **16**, 554.

<sup>117</sup> *Amer. Soc. Test. Mat.*, 1945, *Bull.* 134, 27.

<sup>118</sup> *Mod. Plastics*, 1944, **22**, No. 4, 153.

<sup>119</sup> *Proc. Amer. Soc. Test. Mat.*, 1944, **44**, 1027; *Mod. Plastics*, 1944, **22**, No. 8, 145; C., 1945, 300.



D. A. Shinn,<sup>120</sup> who has reported the results of Izod and Charpy impact strength measurements on a range of cellulose acetate, cellulose acetate butyrate, and ethylcellulose compositions at temperatures between  $-60^{\circ}$  and  $60^{\circ}$ . The theoretical relationship between molecular structure and impact strength has been dealt with by D. R. Morey<sup>121</sup> in terms of different bond types with varying relaxation times which change their relative contributions to mechanical behaviour as the rate of deformation varies between the extremes of static loading and impact testing. Brittleness is considered to result when the bonds have similar relaxation times and extensibilities whereas a broad distribution of such values promotes toughness. The influence of the method of preparation on the results obtained with injection-moulded impact-test specimens has been systematically investigated by R. H. Ball, C. E. Leyes, and A. A. Melnychuk<sup>122</sup>; the injection-cylinder temperature was found to be the most critical factor of those examined, die temperature and moulding cycle having comparatively little effect.

Several improvements have been described in methods for measuring the flow properties of thermoplastics. Details of an attractive and simple extrusion plastometer of wide applicability have been published by H. K. Nason,<sup>123</sup> the standard apparatus for the A.S.T.M. heat-distortion test<sup>124</sup> has been modified to give more consistent results,<sup>125</sup> and G. A. Heirholzer and R. F. Boyer<sup>126</sup> have developed an automatic apparatus for recording temperature-deformation behaviour. Modifications have also been proposed in connexion with the A.S.T.M. method<sup>127</sup> for measuring the light transmission of transparent plastics.<sup>128</sup>

An improved method for the analysis of cellulose acetate and mixed esters has been described by C. J. Malm, L. B. Genung, R. F. Williams, and M. A. Pile,<sup>129</sup> in which the derivative is saponified in solution.

<sup>120</sup> *Mod. Plastics*, 1944, **22**, No. 11, 145.

<sup>121</sup> *Ind. Eng. Chem.*, 1945, **37**, 255; B., 1945, II, 187.

<sup>122</sup> *Ibid.*, 240; B., 1945, II, 186.

<sup>123</sup> *J. Appl. Physics*, 1945, **16**, 338; C., 1946, 142.

<sup>124</sup> A.S.T.M. Designation 648—44T.

<sup>125</sup> J. A. Sauer, F. A. Schwertz, and D. L. Worf, *Mod. Plastics*, 1945, **22**, No. 7, 153; B., 1945, II, 382.

<sup>126</sup> *Amer. Soc. Test. Mat.*, 1945, *Bull.* 134, 37.

<sup>127</sup> A.S.T.M. Designation 672—44T.

<sup>128</sup> E. Diliberti and D. H. Kallas, *Mod. Plastics*, 1945, **22**, No. 8, 150; C., 1946, 141.

<sup>129</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 501; C., 1945, 25.



# RESINS, DRYING OILS, VARNISHES, AND PAINTS.

## NATURAL AND SYNTHETIC RESINS.

By D. H. HEWITT, M.A., A.R.I.C.,

*Lewis Berger and Sons, Ltd.*

NATURAL and synthetic resins continue to be developed along the main lines indicated in the last Report. Natural products are increasingly used to furnish intermediates rather than final ingredients for film-forming compositions. Proliferation of synthetic resins of the accepted types has been accompanied by the evolution of new species.

These latter developments, which include the acetylenic derivatives due to Reppe and the urethane reaction as extended by Bayer, have arisen over the last few years, but receive special mention now owing to the recent release of an accumulation of information, obtained by the British and Combined Intelligence Objectives Sub-Committees, and from secret patents.

At a time when research is turning from the purely utilitarian objectives of war to a broader outlook, it is interesting to record two conceptions which may be considerably elaborated in the near future. The first concerns the latent, but by no means dormant, interest in the possibility of combining chromophoric molecules in polymeric units. This hinterland between dyestuffs and resins has not received the attention due to it, probably because the immense scope of each subject has tended to keep research within rather water-tight compartments. It is surely right for these two fields to overlap in the surface coatings industry and to expect, therefore, that further developments may be expected from this quarter.

Limited success has hitherto attended efforts to obtain useful organic-inorganic polymers having film-forming properties. The silicone resins have redirected attention to this extensive and unexplored territory, and it is to be anticipated that further types will be forthcoming to take our industry a stage further towards, *inter alia*, the conception of a liquid vitreous enamel.

### NATURAL RESINS.

The prospect of synthetic resins, especially of the alkyd type, becoming in easier supply in this country renews interest in their comparison with natural resins with particular regard to performance against cost.<sup>1</sup>

#### *Fossil Resins.*

The elucidation of fossil resin structure makes slow progress. A

<sup>1</sup> H. R. Touchin, *Paint Manuf.*, 1945, 15, 158; B., 1945, II, 348.



report has become available of recent studies by H. Janistyn<sup>2</sup> on the composition of amber in which he used chromatographic analysis to separate the sterol compounds. M. Nierenstein<sup>3</sup> has added another, viz., *l*-leucomaclurin glycol ether, to the characterised constituents of kauri gum.

E. Mertens and L. Hellinckx<sup>4</sup> have turned their attention to the hydrogenation cracking of Congo copal. Substituted aromatic and hydroaromatic compounds formed the bulk of their volatile product.

There is increasing support for the economy and performance of lightly run Congo copal in varnish making. A comprehensive report by the New York Paint and Varnish Production Club<sup>5</sup> describes the testing of several types of varnish and enamel made from plant batches of slack-melt gum. Such varnishes are often both lower in viscosity and faster-drying than, but equally as durable as, their counterparts made from fully run gum.

### Shellac.

The closing of the London Shellac Research Bureau signifies the end of a particular series of technical papers, bulletins, and memoranda which have been a valuable guide to many workers in this field and to all users of the commodity itself. The latter particularly will have benefited by two recent papers<sup>6</sup> on the storage of lacs and their reconditioning, together with recommendations regarding the determination of volatile content.<sup>7</sup>

B. S. Gidvani<sup>8</sup> has reviewed recent research work in this field. Among current developments are to be included the results of his own investigations with N. R. Kamath into the use of lac with ethylcellulose<sup>9</sup> and into the applications for lac esters as plasticisers for nitrocellulose<sup>10</sup> and urea-formaldehyde<sup>11</sup> resins. Further information regarding lac-melamine resins with and without formaldehyde has been made available.<sup>12</sup>

G. N. Bhattacharya has analysed the dielectric properties of lac<sup>13</sup> and compared them with those of dammar and mastic.<sup>14</sup> The results are tentatively discussed in relation to chemical constitution, but further elucidation is obviously desirable.

<sup>2</sup> *Fette u. Seifen*, 1941, **48**, 501; *Seifens.-Ztg.*, 1942, **69**, 123.

<sup>3</sup> *Pharm. J.*, 1944, **153**, 5; *B.*, 1945, II, 60.

<sup>4</sup> *Chim. Peint.*, 1942, **5**, No. 1, 28.

<sup>5</sup> *Off. Digest*, 1944, No. 240, 531.

<sup>6</sup> M. Rangaswami and S. C. De, *Indian Lac Res. Inst.*, 1944, *Bull.* 56; *B.*, 1945, II, 59. N. R. Kamath and B. S. Gidvani, *London Shellac Res. Bur.*, 1944, *Tech. Paper* 25; *B.*, 1945, II, 26.

<sup>7</sup> *Ibid.*, 1945, *Bull.* 7; *C.*, 1945, 109.

<sup>8</sup> B. S. Gidvani, *J. Oil Col. Chem. Assoc.*, 1945, **28**, 83; *B.*, 1945, II, 277.

<sup>9</sup> *London Shellac Res. Bur.*, 1945, *Tech. Paper* 27; *B.*, 1945, II, 188.

<sup>10</sup> *Paint Manuf.*, 1945, **15**, 93; *B.*, 1945, II, 279.

<sup>11</sup> *Paint Tech.*, 1945, **10**, 35; *B.*, 1945, II, 145.

<sup>12</sup> Y. Sankaranarayanan and H. K. Sen, *Indian Lac Res. Inst.*, 1944, *Bull.* 57; *B.*, 1945, II, 26.

<sup>13</sup> *Indian J. Physics*, 1944, **18**, 1; *A.*, 1945, I, 10.

<sup>14</sup> *Ibid.*, 159; also *Indian Lac Res. Inst.*, 1944, *Bulls.* 59—61; *A.*, 1945, I, 185.



The polymerisation of lac has been studied by S. R. Palit.<sup>15</sup> H. H. Bassford, jun., and W. H. Gardner<sup>16</sup> claim the product of esterification with diamines, whilst both they<sup>17</sup> and G. M. Ajmani<sup>18</sup> describe the further reaction of shellac-rosin esters with alcohols and with cashew nutshell liquid respectively.

*Rosin and its Derivatives.*

I. Hatfield reports<sup>19</sup> further experiments regarding the increased flow of oleoresin from the pine by chemical and physical stimulation. This process was exploited by Hessenland to increase German rosin production during the war. A. Möller<sup>20</sup> gives physical and chemical details of the two resulting grades which were made available and claims that the incomplete removal of these chemical stimulants prior to distillation caused a high abietic content with a resultant tendency to crystallisation and cloudiness.

W. Sandermann<sup>21</sup> confirms that the former is aggravated by the presence of abietic and *l*-pimaric acids, but S. R. W. Martin<sup>22</sup> disagrees that optical activity is a reliable criterion of varnish suitability. Martin also discusses the reaction mechanism of heat-treatment which is of particular interest in view of efforts to obtain useful products by controlled decarboxylation.<sup>23</sup>

The trend towards the production of new resin derivatives is further illustrated by a series of patents<sup>24</sup> in which the Hercules Powder Company describe the isolation and further reaction of two dihydroabietic acids. The increasing use of rosin as a resin ingredient rather than as a primary film-forming material is clearly reviewed by F. G. Oswald.<sup>25</sup> Interest during the past year has been focussed on esters. Thus, R. P. Carter<sup>26</sup> traces the stages in the manufacture of such products from the laboratory to the works scale. Hercules Powder Company claim<sup>27</sup> further refinements in the product of esters from rosin and treated rosins. Further attempts to produce harder "ester gums" include the use of polyallyl alcohol<sup>28</sup> and of substantially pure dimeric rosin<sup>29</sup> as ester components. The reaction of rosin esters with metallic sodium and magnesium gives rise to interesting products.<sup>30</sup>

<sup>15</sup> *J. Indian Chem. Soc. (Ind. Ed.)*, 1944, 7, 29; B., 1945, II, 26.

<sup>16</sup> U.S.P. 2,371,212.

<sup>17</sup> U.S.P. 2,371,235.

<sup>18</sup> *J. Sci. Ind. Res., India*, 1945, 3, 354; B., 1945, II, 187.

<sup>19</sup> *Canad. Paint and Var. Mag.*, 1944, 18, No. 9, 16.

<sup>20</sup> *Farve og Lak*, 1945, No. 20, 3; B., 1945, II, 382.

<sup>21</sup> *Fette u. Seifen*, 1943, 50, 273.

<sup>22</sup> *Paint Manuf.*, 1945, 15, 8; B., 1945, II, 145.

<sup>23</sup> Ridbo Laboratories, U.S.P. 2,352,172—3.

<sup>24</sup> U.S.P. 2,360,204—7.

<sup>25</sup> *Off. Digest*, 1944, No. 239, 458; B., 1945, II, 223.

<sup>26</sup> *Ind. Eng. Chem.*, 1945, 37, 448; B., 1945, II, 277.

<sup>27</sup> U.S.P. 2,369,109.

<sup>28</sup> American Cyanamid Co., U.S.P. 2,376,504.

<sup>29</sup> Hercules Powder Co., U.S.P. 2,375,753.

<sup>30</sup> *Idem*, U.S.P. 2,362,888.



The extraction, hardening, and improvement of rosin continue to receive attention. Hercules Powder Company have continued their investigations into one- and two-phase solvent refining processes.<sup>31</sup> They also claim the use of aromatic sulphonic acids as polymerisation catalysts.<sup>32</sup> Ellis-Foster Company describe a process for the polymerisation of crude gum.<sup>33</sup> The Albert Company disclose a process for hardening rosin with formaldehyde.<sup>34</sup> The hydrogenation of rosin in the presence of polar and non-polar solvents<sup>35</sup> gives rise to difficulties owing to the presence of residual catalysts and several measures to overcome these have been described.<sup>36</sup>

### PHENOL-FORMALDEHYDE RESINS.

A steady state of active development appears to have been reached in this field. Further work has been in progress in an attempt to finalise the mechanism of resin formation with particular reference to heat hardening. The intermediate formation of phenol alcohols is further confirmed by I. W. Ruderman,<sup>37</sup> who isolated them from exhaust stacks used in conjunction with alkali-catalysed resins. A. Zinke<sup>38</sup> adduces further evidence to support the reaction of such substances below 170° to yield polyethers which subsequently lose formaldehyde to form methylene bridges. E. Schauenstein and S. Bontempo<sup>39</sup> have correlated hardening temperature with molecular weight viscosimetrically and show that a critical change occurs between 150 and 180°. Experiments by J. B. Niederl and I. W. Ruderman<sup>40</sup> on the reaction of such alcohols with specially "blocked" phenol were inconclusive.

The reaction between phenolic resins and drying oils has been reviewed by T. N. Mehta<sup>41</sup> and E. Fonrobert.<sup>42</sup> The Bakelite Corporation treat novolaks with drying oils in the presence of acid catalysts.<sup>43</sup>

The ingredients for phenolic varnish resins remain substantially unchanged. W. Simpson has reviewed the synthesis of complex phenols<sup>44</sup> for which A. Drinberg has used peat-tar phenols as intermediates.<sup>45</sup> Unsaturated resinous substances which may be used as substituents include acetylene polymers<sup>46</sup> and aromatic petroleum residues.<sup>47</sup> In

<sup>31</sup> U.S.P. 2,324,223, 2,325,410; B., 1945, II, 316.

<sup>32</sup> U.S.P. 2,375,618.

<sup>33</sup> U.S.P. 2,368,165.

<sup>34</sup> G.P. 742,209.

<sup>35</sup> Hercules Powder Co., U.S.P. 2,346,793, 2,346,920—1.

<sup>36</sup> *Idem*, U.S.P. 2,361,213, 2,363,252.

<sup>37</sup> *J.S.C.I.*, 1945, **64**, 204; B., 1945, II, 348.

<sup>38</sup> *Ber.*, 1944, **77**, [B], 264.

<sup>39</sup> *Ibid.*, 1943, **76**, [B], 75; B., 1945, II, 60.

<sup>40</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 1176; A., 1945, II, 396.

<sup>41</sup> *Paint, Oil & Chem. Rev.*, 1944, **107**, No. 9, 9; No. 15, 9; No. 16, 12; No. 17, 14; 1945, **108**, No. 1, 18; B., 1945, II, 277.

<sup>42</sup> *Fette u. Seifen*, 1943, **50**, 514.

<sup>43</sup> B.P. 570,367; B., 1945, II, 351.

<sup>44</sup> *Paint Tech.*, 1944, **9**, 267.

<sup>45</sup> With P. P. Kretschko, *J. Appl. Chem. Russ.*, 1944, **17**, 458; B., 1945, II, 348.

<sup>46</sup> U.S.P. 2,322,990; B., 1945, II, 226.

<sup>47</sup> E. F. McTaggart and H. H. Chambers, B.P. 571,246; B., 1945, II, 388.



the latter case the products are oil-soluble under certain conditions. Imperial Chemical Industries condense the dialcohol product with aliphatic aldehydes.<sup>48</sup>

C. I. Spirk has described<sup>49</sup> modern methods of producing rosin-modified resins of this type, whilst P. O. Powers<sup>50</sup> suggests new techniques for incorporating harder grades into drying oils. Hercules Powder Company claim<sup>51</sup> a very hard, oil-soluble resin from substituted phenols and formaldehyde with rosin, maleic anhydride, and pentaerythritol.

The only interesting development in cold-hardening phenolic resins relates to the use of resorcinol to overcome the necessity for acid catalysis on surfaces such as metals to which they are harmful.<sup>52</sup>

Interest in cashew nutshell liquid resins was stimulated by an announcement of their availability in this country.<sup>53</sup> D. Wasserman and C. R. Dawson<sup>54</sup> have reviewed the constituents of the liquid as it occurs in nature and compared them with those of the commercially available materials, assigning tentative structures to each.

### AMINOPLASTS.

#### *Urea- and Melamine-Formaldehyde Resins.*

In a recent survey J. Hofton<sup>55</sup> has stated the present position regarding the use of conventional types in the surface coating field. J. A. Hadreck<sup>56</sup> has also covered this ground from a more purely technological point of view. In general, there are few significant developments to report.

A one-stage method of making urea-lacquer resins in acid conditions<sup>57</sup> accelerates production and is more convenient to operate than the conventional process. The Plaskon Company report<sup>58</sup> an improved method of incorporating acid catalysts in powdered urea resins, the whole being capable of giving hard films after application from aqueous solution.

The use of melamine continues to receive considerable attention,<sup>59</sup> but its use for lacquer purposes follows similar lines to those already applied to urea, such as modification with glycol.<sup>60</sup>

A continuing tendency is the utilisation of new amine reaction ingredients in these reactions. Thus, Du Pont de Nemours & Co. claim semicarbazide,<sup>61</sup> whilst the General Electric Company continue to develop the use of modified pyrimidyl sulphides.<sup>62</sup>

<sup>48</sup> U.S.P. 2,364,192.

<sup>49</sup> *Chem. Listy*, 1943, 37, 46.

<sup>50</sup> *Ind. Eng. Chem.*, 1944, 36, 1008; B., 1945, II, 60.

<sup>51</sup> U.S.P. 2,380,192.

<sup>52</sup> P. H. Rhodes, *Chem. Met. Eng.*, 1944, 51, No. 12, 196.

<sup>53</sup> J. D. Morgan, *J. Oil Col. Chem. Assoc.*, 1945, 28, 65; B., 1945, II, 247.

<sup>54</sup> *Ind. Eng. Chem.*, 1945, 37, 396; B., 1945, II, 243.

<sup>55</sup> *Chem. and Ind.*, 1944, 410; B., 1945, II, 60.

<sup>56</sup> *Paint, Oil & Chem. Rev.*, 1945, 108, No. 14, 10; B., 1945, II, 348.

<sup>57</sup> American Cyanamid Co., U.S.P. 2,361,715.

<sup>58</sup> B.P. 564,762; B., 1945, II, 30.

<sup>59</sup> J. Olsson, *The Svedberg (Mem. Vol.)*, 1944, 344; B., 1945, II, 145.

<sup>60</sup> Reichhold Chemicals, U.S.P. 2,358,276.

<sup>61</sup> B.P. 567,838.

<sup>62</sup> B.P. 569,413-5; B., 1945, II, 318. B.P. 570,520, 570,569; B., 1945, II, 351.



*Amide Resins.*

The development of nylon in a soluble form generally suitable for coatings appears still to be in the laboratory stage.<sup>63</sup> A new method of dispersion has been proposed<sup>64</sup> to overcome this solubility problem.

Meanwhile further information has become available regarding the Norelac resin mentioned in the last Report. L. B. Falkenburg and his colleagues have extended their work<sup>65</sup> whilst A. G. Hovey provides useful, independent experience on their technological evaluation.<sup>66</sup>

*Urethanes.*

Although German developments in super-polyamides have been considerable,<sup>67</sup> particular interest has been aroused by the publication of reports regarding the use made of the urethane reaction by Bayer and his colleagues at Leverkusen. In general, the reaction between hydroxylated compounds and *iso*(thio)cyanic acid derivatives, giving rise to peptide linkages, has widespread application in surface coatings, as witness a number of recent patents. Thus, mono-, di-, or poly-*iso*-(thio)cyanates (carbimides or thiocarbimides) may be condensed with unsaturated fatty esters of polyhydric alcohols,<sup>68</sup> polymerised or oxidised drying oils,<sup>69</sup> varnishes,<sup>70</sup> or alkyd resins<sup>71</sup>; the presence of the usual driers has a catalytic effect on this reaction.<sup>72</sup> The phenolic hydroxyl group may also be made to react in the same way.<sup>73</sup>

The chief practical application appears to be in the cross-linking of polymeric esters having even a small degree of unreacted hydroxylation. Thus, small percentages of polyisocyanates effectively "cold-harden" normal types of alkyd resin.

## ALKYD RESINS.

At a time when consumption of this type of film-forming material resumed an upward trend, several authors<sup>74</sup> have reviewed methods of manufacture and possible developments in formulation arising from the availability of new materials. N. A. Kozulin<sup>75</sup> has proposed to introduce phthalic anhydride into the reaction mixture continuously as a vapour.

Lively interest continues to be shown in formulations based on maleic anhydride and W. L. Faith<sup>76</sup> has continued his investigations into new

<sup>63</sup> E. I. Du Pont de Nemours & Co., B.P. 535,262; B., 1941, II, 201.

<sup>64</sup> *Idem*, U.S.P. 2,342,387.

<sup>65</sup> *Oil and Soap*, 1945, 22, 143; B., 1945, II, 310.

<sup>66</sup> *Mod. Plastics*, 1945, 22, No. 9, 125, 192.

<sup>67</sup> W. Gaade, *Chem. Weekblad.*, 1943, 40, 182, 199.

<sup>68</sup> I.G. Farbenind., G.P. 738,254.

<sup>69</sup> *Idem*, Belg.P. 445,793.

<sup>70</sup> Du Pont, U.S.P. 2,358,475.

<sup>71</sup> Duco A.-G., G.P. 740,266.

<sup>72</sup> Du Pont, U.S.P. 2,374,136.

<sup>73</sup> I.G. Farbenind., G.P. 737,951. Du Pont, U.S.P. 2,349,756.

<sup>74</sup> D. H. Hewitt, *Paint Tech.*, 1945, 10, 5, 29. J. Scheiber, *Fette u. Seifen*, 1943, 50, 12. C. D. Thurmond, *Off. Digest*, 1945, No. 245, 181; B., 1945, II, 383.

<sup>75</sup> Russ.P. 58,181.

<sup>76</sup> *Ind. Eng. Chem.*, 1945, 37, 438; B., 1945, II, 289.



sources of this material. The various methods by which unsaturated dibasic acids can be incorporated in alkyds continue to be demonstrated in the literature.<sup>77</sup> Current examples include the formation of adducts with drying oil radicals<sup>78</sup> and the reaction with alcoholysed drying oils.<sup>79</sup> The Du Pont Company suggest<sup>80</sup> a useful method of controlling the reaction in the polyhydric alcohols in the presence of an inert solvent. Reactive solvents, such as butanol, may also be used.<sup>81</sup>

Among saturated dibasic acids, methylenedisalicylic acid is newly available in the United States.<sup>82</sup> The reaction between butadiene and carbon dioxide in the presence of metallic sodium provides a novel source of materials of the same class.

Pentaerythritol continues to receive serious attention in this country,<sup>83</sup> and at least one commercial formulation based on it was released during the year. Trimethylolpropane has become available in the United States.<sup>84</sup> C. W. Lenth and R. N. DuPuis<sup>85</sup> give an interesting account of the hydrogenolysis of sugars to give products (including glycerol) suitable for alkyd resin production. A process for the production of polyallyl alcohol by the alcoholysis of suitable polyallyl esters appears to yield a more suitable product<sup>86</sup> than the straight polymerisation of the monomeric alcohol under conditions so far described.<sup>87</sup>

The tendency towards the incorporation of unsaturated molecules was noted in the last report. Recent disclosures include the use of furylacrylic acid,<sup>88</sup> which is available on the development scale in this country, and copolymers including such molecules as divinylbenzene.<sup>89</sup>

The alkyd-urea-formaldehyde combination is of proved value in coatings to resist abrasion and now shows promise in textile applications. A novel process of combining these two involves emulsifying the resin in a continuous phase containing water-soluble urea alcohols.<sup>90</sup>

H. J. Wright and R. N. DuPuis<sup>91</sup> show that extraction of alkyd resins with alcohol gives products which dry more rapidly than the original material. The extracted portion is slow-drying, but might be used as a plasticiser.

<sup>77</sup> J. de Buigne, *Rev. Prod. Chim.*, 1944, **47**, No. 9—10, 65.

<sup>78</sup> Imperial Chemical Industries, B.P. 565,431. Noury & van der Lande, Belg.P. 493,330.

<sup>79</sup> Glidden Co., U.S.P. 2,369,683.

<sup>80</sup> U.S.P. 2,370,962.

<sup>81</sup> Beckacite Kunsthartzfabrik, F.P. 880,082.

<sup>82</sup> J. A. Lee, *Chem. Met. Eng.*, 1945, **52**, No. 2, 155.

<sup>83</sup> S. R. W. Martin, *Paint Manuf.*, 1945, **15**, 89; B., 1945, II, 277.

<sup>84</sup> *Rubber Age*, 1944, **56**, 202.

<sup>85</sup> *Ind. Eng. Chem.*, 1945, **37**, 152; B., 1945, II, 161.

<sup>86</sup> Shell Development Co., B.P. 565,719; B., 1945, II, 70.

<sup>87</sup> *Idem*, B.P. 566,344.

<sup>88</sup> Imperial Chemical Industries, B.P. 569,525; B., 1945, II, 317.

<sup>89</sup> General Electric Co., U.S.P. 2,340,109.

<sup>90</sup> British Industrial Plastics, B.P. 568,388; B., 1945, II, 226.

<sup>91</sup> *Ind. Eng. Chem.*, 1944, **36**, 1004; B., 1945, II, 60.



## ETHENOID POLYMERS.

Once again it is possible to report great activity in this field.

*Resins from Unsaturated Hydrocarbons and their Derivatives.*

The usefulness of polymerised hydrocarbons for coatings has recently been reviewed briefly.<sup>92</sup> This is topical in view of the trend to examine the resin-forming characteristics of crude fractions from the coal tar and petroleum industries. M. A. Stepanenko and A. E. Minskaja<sup>93</sup> have described a method for polymerising the coal-tar xylene fraction containing styrene, indene, and coumarone. Dorman, Long & Co. describe similar processes in a series of patents.<sup>94</sup> The United Gas Improvement Co. have concentrated on the utilisation of light oil fractions.<sup>95</sup>

Polymers and copolymers of dichlorostyrene have greater heat-resistance than the corresponding styrene polymers, while retaining similar physical and chemical properties.<sup>96</sup>

Acyclic terpenes such as myrcene may be treated with maleic anhydride to yield products capable of forming the usual soaps and esters.<sup>97</sup> Alternatively, they may be copolymerised with unsaturated fatty acid esters with or without Fredel-Crafts catalysts.<sup>98</sup> In the presence of the latter dipentene may be copolymerised with vinyl chloride<sup>99</sup> or with alicyclic hydrocarbons.<sup>100</sup>

*Acrylic Acid Polymers.*

D. A. Rothrock has reviewed their applications in the coatings industry.<sup>101</sup> New esters include those derived from terpene alcohols<sup>102</sup> and from polyhydric alcohols of the carbohydrate series.<sup>103</sup> I.G. Farbenindustrie have described a series of diacrylic diamides of the nature of crystalline solids which readily polymerise on heating.<sup>104</sup>

*Allyl Polymers.*

Although the first allyl plastic was commercialised as recently as 1942, developments are being revealed which suggest that allyl polymers may become of the first importance in surface coatings. Prepolymerised diallyl phthalate, which may be regarded as a solution of *B*-stage resin

<sup>92</sup> O. C. Slotterbeck and D. W. Young, *Off. Digest*, 1944, No. 240, 511.

<sup>93</sup> *Koks i Khim.*, 1941, 11, No. 5, 29.

<sup>94</sup> B.P. 549,516, 550,798, 574,020; B., 1943, I, 102; 1943, II, 128; 1946, II, 179.

<sup>95</sup> U.S.P. 2,317,857—9; B., 1945, II, 119. U.S.P. 2,373,866.

<sup>96</sup> J. C. Michalek and C. C. Clark, *Chem. Eng. News*, 1944, 22, 1559; B., 1945, II, 84.

Mathieson Alkali Works, B.P. 564,828—9; B., 1945, II, 7, 30; B.P. 570,596; B., 1945, II, 313.

<sup>97</sup> Hercules Powder Co., U.S.P. 2,347,970, 2,348,575.

<sup>98</sup> *Idem*, U.S.P. 2,370,689.

<sup>99</sup> *Idem*, U.S.P. 2,354,775.

<sup>100</sup> *Idem*, U.S.P. 2,348,565.

<sup>101</sup> *Canad. Chem.*, 1944, 28, 599; B., 1945, II, 25.

<sup>102</sup> Wingfoot Corp., U.S.P. 2,363,044.

<sup>103</sup> R. H. Treadway and E. Yanovsky, *J. Amer. Chem. Soc.*, 1945, 67, 1038; A., 1945, II, 312.

<sup>104</sup> Belg.P. 445,606.



in the monomer, may be used as a vehicle for stoving finishes.<sup>105</sup> The monomer may be copolymerised with castor oil under conditions which dehydrate the latter to yield an internally plasticised polymer of the same type.<sup>106</sup> The diallyl esters of dimeric fatty acids do not, however, hold the same promise of future utility.<sup>107</sup> A trend is noteworthy towards the development of more complex allyl esters<sup>108</sup> as film-forming materials.

### SILICON POLYMERS.

Widespread applications continue to be made of the silicone resins developed in the United States by the Dow Corning<sup>109</sup> and General Electric<sup>110</sup> concerns. Apart from the original applications in electrical insulation, greases, waxes, and rubbers have been produced.<sup>111</sup> H. A. Gardner and M. W. Westgate describe preliminary experiences with some types more particularly suitable as surface coatings.<sup>112</sup> As a direct result of this development, renewed attention has been focussed on silicon ester polymers.<sup>113</sup>

### ANALYSIS.

Both H. Barron<sup>114</sup> and T. P. G. Shaw<sup>115</sup> have put forward systematic schemes for the identification of synthetic resins. The Chicago Paint and Varnish Production Club<sup>116</sup> have reported on colour reactions for a number of varnish resins. The New York Paint and Varnish Production Club<sup>117</sup> have reviewed the methods of determining solids content, and recommend the use of a vacuum procedure where possible.

<sup>105</sup> British Thomson-Houston Co., B.P. 571,496.

<sup>106</sup> Shell Development Co., Can.P. 423,558—9.

<sup>107</sup> H. M. Teeter and J. C. Cowan, *Oil and Soap*, 1945, 22, 177; B., 1945, II, 378.

<sup>108</sup> Pittsburgh Plate Glass Co., U.S.P. 2,370,569, 2,370,573.

<sup>109</sup> S. L. Bass *et al.*, *Mod. Plastics*, 1944, 22, No. 3, 124; B., 1945, II, 276.

<sup>110</sup> E. G. Rochow, *Chem. Eng. News*, 1945, 23, 612.

<sup>111</sup> *Rubber Age*, 1944, 56, 173; B., 1945, II, 156.

<sup>112</sup> *Nat. Paint Var. Assoc. Circ.* 705.

<sup>113</sup> Plaskon Co., U.S.P. 2,313,678; B., 1945, II, 30. C. Shaw and J. E. Hackford, *Ind. Chem.*, 1945, 21, 130; B., 1945, II, 162.

<sup>114</sup> *Brit. Plastics*, 1944, 16, 339, 460; 17, 56; C., 1945, 109.

<sup>115</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 541; C., 1945, 29.

<sup>116</sup> *Paint, Oil Chem. Rev.*, 1944, 107, No. 22, 72.

<sup>117</sup> *Ibid.*, 11; C., 1945, 241.

## DRYING OILS, DRIERS, AND VARNISHES.

By J. H. GREAVES, B.Sc., A.R.I.C.,

*Messrs. Younghusband, Barnes & Co., Ltd.*

IN a subject dealing with such complex natural products as the drying oils, which in use themselves undergo very complicated changes, scientific progress is necessarily only gradual yet steady. The year under review emphasises this aspect with the two topics which at one and the same time are relatively recent and important, namely, isomerisation and



drying oil pentaerythritol esters. In spite of the continued shortage of linseed and other oils for use as film-forming materials, the subject of conservation of oils has been studied so fully in recent years that little new work has appeared, although tall oil promises to be an important raw material.

### DRYING OILS.

#### *General, Occurrence, and Extraction.*

To an ever-increasing degree the economic position of oils and fats, reviewed by R. M. Walsh,<sup>1</sup> governs their technical investigation and use. A survey of the development of production of oils, including oiticica, flax, and castor, in Brazil, a country with great latent resources, has been given by C. E. Nabuco de Araujo.<sup>2</sup> The Fat Literature Review Committee<sup>3</sup> has published an extensive review of the literature for 1943-44 of all aspects of fats and oils.

In America investigations have been continued on the composition of the oil from different varieties of linseed grown in different districts. H. R. Sallans and G. D. Sinclair<sup>4</sup> have found that both variety and environment affect many of the analytical constants determined, including iodine and thiocyanogen values, but not unsaponifiable matter; statistical analysis of the data obtained gives rise to the following reasonably accurate equations, where CNS V. is the thiocyanogen value and I.V. is the iodine value:  $\text{CNS V.} = 0.44 \times \text{I.V.} + 38.59$ ; % linolenic acid  $= 0.49 \times \text{I.V.} - 37.93$ ; % linoleic acid  $= 0.055 \times \text{I.V.} + 0.73$ ; % oleic acid  $= -0.48 \times \text{I.V.} + 113.08$ . In another paper, by E. P. Painter,<sup>5</sup> covering a similar field of study, the relationship between thiocyanogen value and iodine value is found to be an equation rather different from that just given, namely,  $\text{CNS V.} = 0.496 \times \text{I.V.} + 26.7$ . It is not found possible to calculate the composition of linseed oil in terms of constituent glycerides with such accuracy as the constituent fatty acids (for example, differences in composition exist which are independent of the iodine value), and the following equations are only approximate: % saturated glycerides  $= -0.103 \times \text{I.V.} + 28.9$ ; % oleic glycerides  $= -0.382 \times \text{I.V.} + 91.4$ ; % linoleic glycerides  $= 0.552 \times \text{I.V.} - 49.1$ . In a comment on these results, P. O. Powers,<sup>6</sup> from general experience, considers that the iodine value is an accurate measure of the performance of an oil, and therefore, presumably, of its fatty acid composition.

R. S. McKinney and co-workers<sup>7</sup> have continued laboratory investigations on the question of obtaining the oil from tung seed, with special

<sup>1</sup> *Oil and Soap*, 1944, **21**, 283; B., 1945, **II**, 115.

<sup>2</sup> *Ind. y Quim.*, 1943, **5**, 46, 53; B., 1945, **II**, 243.

<sup>3</sup> M. M. Piskur, *Oil and Soap*, 1945, **22**, 69, 77; B., 1945, **II**, 244.

<sup>4</sup> *Canad. J. Res.*, 1944, **22**, **F**, 119; B., 1945, **II**, 181.

<sup>5</sup> *Oil and Soap*, 1944, **21**, 343; B., 1945, **II**, 182.

<sup>6</sup> *Ibid.*, 1945, **22**, 52; B., 1945, **II**, 219.

<sup>7</sup> A. F. Freeman, F. C. Pack, and R. S. McKinney, *ibid.*, 1944, **21**, 328; B., 1945, **II**, 142. R. S. McKinney, N. J. Halbrook, and R. E. Oglesbee, *ibid.*, 353; B., 1945, **II**, 182.



reference to optimum moisture content. When a solvent extraction method is used, 7% moisture content is best, while for expression, the seed should contain 4.2% of water and be mixed with 20% of shell. A solvent mixture typified by the acetone-methyl alcohol azeotrope is patented<sup>8</sup> for the extraction of tung oil. A bibliography<sup>9</sup> on solvent extraction up to January, 1944, has been collected. In one patent<sup>10</sup> oil is extracted from the seed by ball-milling in the presence of an aqueous medium followed by centrifuging.

#### *Individual Oils.*

*Linseed Oil.*—When raw oil is heated there is normally precipitated, at about 400° F. or above, the gelatinous material called "break," a decomposition product of the lecithin and allied materials in the oil. The break is removed by various refining methods, including stabilisation (e.g., elimination of all traces of moisture). H. R. Touchin<sup>11</sup> has studied a means of removal of the break by a method used for refining edible oils, namely, treatment with aqueous caustic soda, and finds an equation relating the amount,  $v$ , of soda required to remove the break in a time  $t$  from 100 g. of oil; a constant in the equation varies with the efficiency of the stirring. A patent<sup>12</sup> describes a method for the stabilisation of the break, in which raw oil is led into a pool of oil at 320° C. while a corresponding quantity of oil is withdrawn.

*Dehydrated Castor Oil and Oiticica Oil.*—These two oils, with their contents of conjugated fatty acids, occupy a special position, especially with regard to achieving finishes with special qualities once easily obtained with tung oil. It is significant that whereas dehydrated castor oil is used in ever-increasing quantity, oiticica oil finds little favour. Materials mentioned in the patent literature as catalysts for the dehydration of castor oil include cobalt acetate and other oxide-forming salts,<sup>13</sup> boron oxide and other boron-containing compounds,<sup>14</sup> phosphorus oxychloride, and ethyl sulphate.<sup>15</sup> A method of dehydration described by O. Grummitt and H. Fleming<sup>16</sup> involves 96% acetylation with glacial acetic acid in the presence of 0.1% of *p*-toluenesulphonic acid with continuous removal of the water of reaction; after acetylation the temperature is raised to above 250° with evolution of acetic acid and the formation of the new double bond. Catalytic dehydration in the presence of oiticica oil<sup>17</sup> is used for making a phenolic varnish. This latter oil is apparently improved by heating with boron trifluoride.<sup>18</sup>

<sup>8</sup> Commercial Solvents Corp., U.S.P. 2,320,970; B., 1945, II, 185.

<sup>9</sup> A. C. Beckel, *Oil and Soap*, 1944, 21, 264; B., 1945, II, 83.

<sup>10</sup> Schwarz Engineering Co., U.S.P. 2,325,327; B., 1945, II, 308.

<sup>11</sup> *J. Oil Col. Chem. Assoc.*, 1945, 28, 49; B., 1945, II, 182.

<sup>12</sup> Pittsburgh Plate Glass Co., U.S.P. 2,317,915; B., 1945, II, 245.

<sup>13</sup> Leather Cloth Co., B.P. 563,759; B., 1945, II, 84.

<sup>14</sup> Baker Castor Oil Co., U.S.P. 2,317,361; B., 1945, II, 275.

<sup>15</sup> S. Kellogg & Sons, U.S.P. 2,330,180; B., 1945, II, 379.

<sup>16</sup> *Ind. Eng. Chem.*, 1945, 37, 485; B., 1945, II, 306.

<sup>17</sup> H. A. Gardner, jun., U.S.P. 2,318,304; B., 1945, II, 143.

<sup>18</sup> Socony-Vacuum Oil Co., U.S.P. 2,316,187; B., 1945, II, 25.



*Isano Oil* has been adequately reviewed by G. T. Bray.<sup>19</sup> This reddish-yellow rather viscous oil, also called "n'gore" and "ongueko" oil, occurs to the extent of 58—78% in the kernels of *Ongokea klaineana* Pierre. Isanic acid, a main constituent, found by A. Steger and J. van Loon<sup>20</sup> to contain two acetylenic linkings and one vinyl group, renders the oil too reactive to be heated alone to stand oil-making temperatures; indeed, by itself, the drying properties are poor, and it is most suitably used by heat-treatment in admixtures with non-conjugated drying oils.<sup>21</sup> The drying powers of these are stated to be improved by such a process.

*Tall Oil*,<sup>22</sup> a by-product of the paper pulp industry, has had attention focussed on it by the world-wide shortage of oils and fats. The crude material, sometimes termed liquid rosin, may be refined in a variety of ways, including washing with aqueous solutions and extraction by organic solvent, along with bleaching by fuller's earth.<sup>23</sup> Besides the sources used by Germany in recent years, chiefly Sweden, tall oil is also available in large quantities in North America. In general, a slightly refined tall oil consists of roughly 45% of fatty acids, 45% of so-called rosin acids, and 10% of unsaponifiable matter. The resin acids, which tend to crystallise, can be partly removed by filtering or distillation. R. H. Anderson and D. H. Wheeler<sup>24</sup> in an analysis of crude and refined tall oils find that the content of fatty acids to be 26—45% and 61% respectively, and the rosin acids 38—46% and 32% respectively. The fatty acids averaged linoleic 48%, oleic 45%, and saturated acids 7%. Part of the linoleic acid was conjugated, probably due to isomerisation by alkali during the recovery process. W. H. Jennings,<sup>25</sup> when considering possible uses in various industries, includes the manufacture of alkyd resins. There is no doubt that tall oil has potentially great and varied applications in the drying oil industry.

*Other Oils*.—Analytical figures have been published for tumbling mustard seed oil<sup>26</sup> (Wijs iodine value 151), Néou oil<sup>27</sup> (linoleic acid 34.5%, elæostearic acid 28.2%), and for the component fatty acids of niger-seed and stillingia oils.<sup>28</sup>

### *Modified Oils.*

By the term modification of a drying oil is here understood a treatment of the oil other than by well-known and standardised processes such as stand oil manufacture and air-blowing. It is usually possible to recognise modification as belonging to one (or more) of three classes, according to

<sup>19</sup> *Bull. Imp. Inst.*, 1944, **42**, 250; B., 1945, II, 142.

<sup>20</sup> *Fette u. Seifen*, 1937, **44**, 243; B., 1937, 1080.

<sup>21</sup> N. V. Industr. Maats. v./h. Noury & van der Lande, B.P. 516,024; B., 1940, 292.

<sup>22</sup> K. B. Edwards, *Chem. and Ind.*, 1942, 233; B., 1942, II, 294.

<sup>23</sup> Hercules Powder Co., U.S.P. 2,315,584 and 2,316,499; B., 1945, II, 24.

<sup>24</sup> *Oil and Soap*, 1945, **22**, 137; B., 1945, II, 306.

<sup>25</sup> *Paper Trade J.*, 1945, **120**, *TAPPI Sect.*, 185; B., 1945, II, 244.

<sup>26</sup> W. H. Goss and J. E. Ruckman, *Oil and Soap*, 1944, **21**, 234; B., 1945, II, 23.

<sup>27</sup> N. Ivanoff, *Bull. Soc. chim.*, 1944, [v], **11**, 404; B., 1945, II, 378.

<sup>28</sup> C. R. Pye, *Paint Tech.*, 1945, **10**, 113; B., 1945, II, 273.



whether the process affects the triglyceride as a whole, the fatty acid chain, or the polyalcohol radical. Sometimes the treatment is properly a refining treatment, as when antioxidants are removed with nitric acid<sup>29</sup>; at other times the mode of action can only be guessed at, as when the improvement in the drying power of semi-drying and drying oils is stated to occur when they are heated at 200—250° with 0.1% of an alkali.<sup>30</sup>

*Triglyceride Modification.*—New solvents for segregation continue to be described; for example, nitromethane and certain other organic nitro-compounds<sup>31</sup> are stated preferentially to extract unsaturated glycerides.

*Fatty Acid Modification.*—Little new has been published concerning technical preparation of oils conjugated by alkali treatment. A paper by J. E. Good<sup>32</sup> dealing with synthetic drying oils mentions that an isomerised linseed oil is being manufactured, but is concerned almost exclusively with a description of dehydrated castor oil. The movement of double bonds to the conjugated position due to oxygen has again been described, this time by J. L. Bolland and H. P. Koch,<sup>33</sup> who find that ethyl linoleate becomes at least 70% conjugated under certain conditions. Heat-treatment of linseed oil fatty acids with activated alumina<sup>34</sup> gives rise to 35% conjugation, but it must be pointed out that neither of these conjugation processes bears any necessary relation to the problem of improvement of drying properties. Attention has been drawn to the ease with which volatile fatty acids in a triglyceride can be replaced by less volatile acids by heating in vacuum.<sup>35</sup>

*Alcohol Modification.*—The interest shown in recent years in polyhydric alcohols other than glycerol has given rise to the necessity of the study of esterification. In an examination of the reaction kinetics<sup>36</sup> of the esterification of peanut oil fatty acids with glycerol it has been found that tin and zinc chlorides are the best catalysts, and that they reduce darkening. On the other hand, J. C. Konen, E. T. Clocker, and R. P. Cox,<sup>37</sup> when studying the esterification of drying oil fatty acids with sorbitol, mono- and di-pentaerythritol, find that catalysts give no advantage. The best reaction conditions are described as heating the acids with a 5% excess of the alcohol under vacuum at 450° F. in a current of inert gas. Esters prepared in this way showed faster bodying and better alkali- and water-resistance than the corresponding triglycerides, the best being made from certain alcohols (not described) having more than six hydroxyl groups per molecule.

<sup>29</sup> Reichhold Chemicals Inc., U.S.P. 2,196,796; B., 1945, II, 380.

<sup>30</sup> H. E. Adams and P. O. Powers, *Ind. Eng. Chem.*, 1944, 36, 1124; B., 1945, II, 83.

<sup>31</sup> Pittsburgh Plate Glass Co., U.S.P. 2,316,512; B., 1945, II, 58.

<sup>32</sup> *Amer. Ink Maker*, 1944, 22, 34; B., 1945, II, 219.

<sup>33</sup> *J.C.S.*, 1945, 445; A., 1945, II, 310.

<sup>34</sup> A. Turk and P. D. Boone, *Oil and Soap*, 1944, 21, 321; B., 1945, II, 114.

<sup>35</sup> Wecoline Products Inc., U.S.P. 2,182,232; B., 1945, II, 245.

<sup>36</sup> R. O. Feuge, E. A. Kraemer, and A. E. Bailey, *Oil and Soap*, 1945, 22, 202; B., 1945, II, 346.

<sup>37</sup> *Ibid.*, 57; B., 1945, II, 201.



## ANALYSIS.

Even in the determination of the more simple analytical constants of oils there is still much to be done in the way of standardisation. The Oil and Colour Chemists' Association<sup>38</sup> have found that determinations of the acid value of a stand oil by forty different operators give quite large variations, due, it is concluded, to lack of precision in defining end-points. It is suggested that a slight pink colour should persist for at least two minutes after the last addition of alkali, a length of time that would probably be cut down by most titrators. Variations in the saponification values of the same oil were much smaller. For the acid value of a dark-coloured oil, F. S. Robinson<sup>39</sup> recommends boiling with alcohol for 10 minutes to extract the fatty acids<sup>40</sup> and titrating the oil-free alcohol layer after settling; the results are claimed to agree with those obtained potentiometrically. Standard methods suitable for the ordinary laboratory are given by J. A. Cottrell<sup>41</sup> for determining acid, saponification, hydroxyl, carbonyl, and diene values and unsaturation.

D. C. Hu, M. C. Chen, and P. H. Wong<sup>42</sup> find the "oxidation iodine value" by treating the oil in carbon tetrachloride solution with N-sodium dichromate dissolved in acetic acid containing trichloroacetic acid. Stability of Wijs' iodine solution is frequently a subject of discussion, and whereas it is sometimes found to be substantially stable over a considerable period, for example, 505 days, when kept in dark bottles,<sup>43</sup> another worker detects a change in concentration of 0.00006N. per day at 81° F.<sup>44</sup> New information continues to be published which increases our knowledge of spectrographic absorption as an analytical tool. R. H. Barnes, I. I. Rusoff, E. S. Miller, and G. O. Burr<sup>45</sup> have investigated several unsaturated fatty acids and natural fats and give data showing relationship between degree of unsaturation and extinction coefficient at 2100 Å. From the results of investigations on isomerisation experiments with alkali in glycol solution, T. P. Hilditch, R. A. Morton, and J. P. Riley<sup>46</sup> show how a mixture of linolenic, linoleic, oleic, and saturated acids can be analysed by isomerising and then determining extinction coefficients at different wave-lengths.

Chromatographic methods, reviewed by M. R. Mills<sup>47</sup> and F. T. Walker,<sup>48</sup> are finding increasing use for oils. In a mixture of a fat and fatty acids,

<sup>38</sup> N. Strafford, *J. Oil Col. Chem. Assoc.*, 1945, **28**, 97; C., 1945, 242.

<sup>39</sup> *J. S. African Chem. Inst.*, 1944, **27**, 19; C., 1945, 108.

<sup>40</sup> V. L. Kretovitch and A. A. Bundel, *Biochimia*, 1945, **10**, 159; B., 1945, **11**, 346.

<sup>41</sup> *Paint Ind. Mag.*, 1944, **59**, 268; C., 1945, 173.

<sup>42</sup> *J. Chinese Chem. Soc.*, 1943, **10**, 30; C., 1945, 171.

<sup>43</sup> F. A. Norris and R. J. Buswell, *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 417; B., 1945, **11**, 17.

<sup>44</sup> R. Child, *ibid.*, 1945, **17**, 530; C., 1945, 242.

<sup>45</sup> *Ibid.*, 1944, **16**, 385; C., 1945, 28.

<sup>46</sup> *Analyst*, 1945, **70**, 68; C., 1945, 102.

<sup>47</sup> *Paint Tech.*, 1945, **10**, 107; B., 1945, **11**, 274.

<sup>48</sup> *J. Oil Col. Chem. Assoc.*, 1945, **28**, 119; B., 1945, **11**, 306.



the acids may be completely removed by a column of activated alumina,<sup>49</sup> leaving the fat in solution in the percolate. This process can be utilised in the determination of unsaponifiable matter. The Society of Public Analysts' method is carried out up to the point of completing the extraction with ether. The extract is dried, the acids are removed on the column of alumina, and the unsaponifiable matter is recovered from the ether solution and weighed.

Monoglycerides can be determined titrimetrically<sup>50</sup> in mixtures with di- or tri-glycerides or glycol esters by means of periodic acid. Details of the colours given by the Hirschsohn reagent<sup>51</sup> (90% aqueous trichloroacetic acid) with various oils and varnishes have been listed.

<sup>49</sup> N. D. Sylvester, A. N. Ainsworth, and E. B. Hughes, *Analyst*, 1945, **70**, 295; C., 1945, 243.

<sup>50</sup> W. D. Pohle, V. C. Mehlenbacher, and J. H. Cook, *Oil and Soap*, 1945, **22**, 115; C., 1945, 172.

<sup>51</sup> H. C. Brinker, *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 130; C., 1945, 108.

## SOLVENTS.

BY G. E. SMOCK,  
*Howards and Sons Ltd.*

THERE has been no change in the general solvent position this year, and no notable additions to the products already commercially available. Solvent production and consumption in this country are still deplorably dependent on imported materials, but the enormous post-war demand for solvents of all types will undoubtedly provide the necessary stimulus to our own solvent industry.

In the lower-boiling class ethyl, butyl, and amyl alcohols and their acetates have all been extensively used, although still subject to control. The aliphatic ketones have also been restricted because they have to be largely imported, but it is certain that petroleum refiners in this country will follow the lead of the American concerns in the production of these ketones by the cracking of petroleum derivatives.

The surface coating industries have again made good use of the higher-boiling solvents, such as the lactic esters and the cyclohexanol derivatives, which are more fortunately placed with regard to supply, having been manufactured in this country for many years. This fact has resulted in an increased consumption of these solvents during the war years, and both cyclohexanone and methylcyclohexanone have been successfully employed as solvents for polyvinyl chloride.<sup>1</sup> The use of these solvents in surface coatings has always been restricted by reason of their comparatively slow rate of evaporation. It is interesting, therefore, that

<sup>1</sup> B.P. 570,915; B., 1945, II, 385.



C. Cannegieter and A. Kooiker<sup>2</sup> have investigated the suitability of methylcyclohexyl acetate and methylcyclohexanone as substitute materials for butyl and ethyl acetates, and conclude that in the large-scale preparation of nitrocellulose lacquers, it is feasible to use a mixture of 50 parts of butyl acetate and 35 parts of methylcyclohexanone to replace 100 parts of butyl acetate.

New glycol ethers have been mentioned, including the monocyclopentyl ether of ethylene glycol<sup>3</sup> and 2-ethylbutyl "cellosolve" (ethylene glycol  $\beta$ -ethylbutyl ether). The latter has been recommended to replace butyl "cellosolve" as a resin solvent because of its lower water-solubility and higher boiling point.<sup>4</sup>

The nitroparaffins have been shown to possess special advantages as solvents for cellulose acetate, triacetate, and acetobutyrate, thus filling an important gap in the present limited range of solvents for these derivatives.<sup>5</sup>

Considerable progress has been made in the production and application of furfuraldehyde and its derivatives. It is claimed that furfuraldehyde is itself an excellent solvent for cellulose derivatives, vinyl and phenol-formaldehyde resins, but it is admitted that it darkens and polymerises on keeping. Derivatives free from this disadvantage are therefore used, in particular, furfuryl alcohol and tetrahydrofurfuryl alcohol, both obtained by hydrogenation. Their solvent powers, however, are somewhat less.<sup>6</sup>

A study of the literature this year confirms the enormous strides which have been made in petroleum technology during the war years. The future of petroleum hydrocarbons and derivatives in the surface coating industries is discussed by E. M. Toby, jun.,<sup>7</sup> who states that as a result of improvements in distillation and fractionation technique such products as *n*-heptane and hexane are in plentiful supply in America. The higher aliphatic hydrocarbons will also be made available later. In addition a wide range of aromatics can be produced by conversion or aromatisation by catalytic cracking. Numerous references and patents have appeared concerning these conversion processes. Average yields of 75% of toluene are obtained from the cyclisation of pure *n*-heptane, a process described by R. C. Archibald and D. S. Greensfelder.<sup>8</sup> The production of synthetic toluene by the catalytic dehydrogenation of crude methylcyclohexane obtained from petroleum naphtha is also outlined in a patent by the Shell Development Co.<sup>9</sup> Modern methods for the production of

<sup>2</sup> *Verfkroniek*, 1943, **16**, 105; B., 1946, II, 342.

<sup>3</sup> U.S.P. 2,327,053; B., 1945, II, 335.

<sup>4</sup> *Amer. Ink Maker*, 1944, **22**, No. 5, 35.

<sup>5</sup> *Ind. Chem.*, 1945, **21**, 289; B., 1945, II, 202.

<sup>6</sup> *Paint Manuf.*, 1945, **15**, 151; B., 1945, II, 278.

<sup>7</sup> *Off. Digest*, 1944, No. 233, 90; B., 1945, II, 224.

<sup>8</sup> *Ind. Eng. Chem.*, 1945, **37**, 356; B., 1945, II, 234.

<sup>9</sup> B.P. 571,654; B., 1945, II, 365.



industrial alcohol, including the synthesis from ethylene and acetylene, are reviewed by A. E. Williams.<sup>10</sup>

New methods of assessing solvent power continue to be based on viscosity measurements. A review of the different methods has been published<sup>11</sup> in which preference is given to the determination of relative viscosity as a means of comparing solvents in this respect. Relative viscosity is defined as the ratio of the viscosity of a standard solution of a solute in the solvent to the viscosity of the solvent itself.

A new procedure for evaluating hydrocarbons as thinners for coating compositions is described<sup>12</sup> in which the concept of solvency is broadened to include more than simply aromatic content as measured by the kauri-butanol test. A "solvency index" is suggested and defined as the ratio of the viscosity of a standard hydrocarbon solution to the viscosity of the test hydrocarbon solution. The viscosities are expressed in poises and both solutions are to have identical total solids content and identical solute. The "solvency index" can then be used to compare the hydrocarbons or to indicate the order of solvency desired in a new solvent.

E. H. McArdle<sup>13</sup> calls attention to the importance of taking into consideration the number of solvent molecules present in any system. He states that for a given concentration large differences in viscosity reduction can be reasonably explained by the number of molecules of thinner present. He introduces a viscosity factor defined as the product of the log of the relative viscosity and the number of molecules of thinner. This theory is applied to solutions of common solid vehicles in various solvents and practical applications are indicated.

The effect of variations in solvent composition on the solid content of lacquers is shown by means of viscosity-concentration graphs in an interesting paper by W. Koch, H. C. Phillips, and R. Wint.<sup>14</sup> "Active" or "hot-spray" solvent mixtures containing solvents of low molecular weight and certain diluents are used to increase the amount of non-volatiles at sprayable viscosity.

In the analytical field S. Groennings<sup>15</sup> has studied further the method originally developed by Grosse and Wackher<sup>16</sup> of estimating the aromatic content of cracked gasolines by specific dispersion. In this method corrections must be made for the specific dispersion of the olefines present. This correction is shown here to vary considerably with the class of olefine. An estimate of the reliability of the recommended correction factors is presented and, as far as possible, the accuracy of the method is determined experimentally.

The application of the Karl Fisher method to the determination of

<sup>10</sup> *Chem. Age*, 1945, 52, 325.

<sup>11</sup> *Lack u. Farben Z.*, 1944, 35.

<sup>12</sup> *Off. Digest*, 1944, No. 241, 579.

<sup>13</sup> *Ibid.*, 1945, No. 246, 229.

<sup>14</sup> *Ind. Eng. Chem.*, 1945, 37, 82; *B.*, 1945, II, 146.

<sup>15</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 361; *C.*, 1945, 236.

<sup>16</sup> *Ibid.*, 1939, 11, 614.



moisture in Naval Stores products is discussed<sup>17</sup> by V. E. Grotlisch and H. N. Burstein. Certain variations and modifications are recommended in the case of terpene solvents. Results obtained with 26 samples of pine oils and terpene solvents show satisfactory accuracy in determining 0.012—1.04% of water.

A method for the separation of ketones and monohydric alcohols from azeotropic mixtures formed by distillation of atmospheric pressure is presented by E. C. Britton, H. S. Nutting, and L. H. Horsley.<sup>18</sup> Further distillation at a substantially different pressure yields a pure component and a small proportion of a different azeotrope, which is similarly treated. The specific cases of methyl alcohol and acetone and of ethyl alcohol and methyl ethyl ketone are quoted.

<sup>17</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 382; C., 1945, 291.

<sup>18</sup> Assrs. to Dow Chemical Co., U.S.P. 2,324,255; B., 1945, II, 260.

## CELLULOSE ESTER AND ETHER LACQUERS.

By H. L. HOWARD, B.Sc., M.I.CHEM.E., F.R.I.C.

THE outstanding difficulty with which cellulose lacquers have had to contend since their inception has been the relatively low build compared with other film-forming materials commonly used, due to the high viscosity of cellulose esters. The introduction of low-viscosity cellulose nitrate was hailed as a real advance some twenty-five years ago, but on reflexion one may be permitted to doubt whether the degradation of a highly polymeric material to meet the requirements of application is really an advance or the correct line of approach to the problem. Similarly, the loading of lacquers with non-cellulosic material, although it achieves a commercial end and leads to purely technical advance, is rather an avoidance of the real issue—the synthesis of a molecular structure of suitable size and shape and possessing the necessary properties. Until this has been done, the demand for higher and higher build will continue. Thus, W. Koch, H. C. Phillips, and R. Wint,<sup>1</sup> continuing work which was reported last year (*Ann. Repts.*, 1944, **29**, 320), have indicated that since the separate effects of higher solvency, increasing resin content, and the use of lower-viscosity plasticisers are cumulative, quite high solid contents are, in theory, possible with existing materials, the limiting factor being the quality of the film desired. Resin-cellulose ester ratios as high as 2:1 yield quite serviceable products, provided nitrocottons of the lowest viscosity are avoided, and in this way solid contents may be raised to 29.5% without exceeding spraying consistency. By employing hot-spraying technique this figure can be

<sup>1</sup> *Ind. Eng. Chem.*, 1945, **37**, 82; B., 1945, II, 146. See also *Off. Digest*, 1945 No. 242, 35.



raised to 36.5%. J. K. Speicher<sup>2</sup> investigating the relation between temperature and viscosity of such lacquers has arrived at the equation  $\log \eta = \log \eta_1 + 0.0207(T_1 - T)$  and appears to have approached the problem from the same angle with similar results. The advantages of the hot-spraying technique are stressed by A. C. Hopkins,<sup>3</sup> who points out that although the initial set is delayed, the hard-drying time is unaltered. The limiting safe temperature is 160° F., and amyl compounds should be avoided. Durability is unaffected. R. L. Ericson<sup>4</sup> stresses the economic advantages of this technique: films may be doubled in thickness, spraying is 30% faster, and a saving of 30% in the cost of solvents is possible. N. R. Kamath and B. S. Gidvani<sup>5</sup> state that with lac-ethylcellulose lacquers solid contents up to 55% are capable of being sprayed satisfactorily at 70° (158° F.).

The logical extension of this work is to be found in the elimination of all solvent by the application of the fused ester as claimed by the Eastman Kodak Co.<sup>6</sup> Cellulose butyrate and acetate butyrate containing a small amount of plasticiser (5—30%) are applied by roller, spray, or doctor blade at the melting point to paper and other surfaces, which can be embossed while still soft if desired, to form very flexible products. The application of such materials in solution form, allowing to air-dry and then fusing them at 200—250° on to the surface without charring, is covered by a further patent.<sup>7</sup> Good adhesion is obtained in both cases, and sheet metal so coated can be creased and bent to a considerable extent without damage. Where high electrical insulation or water-resistance is required, as with enamelled copper wire, overcoating with cellulose lacquer of the conventional type is possible. Precautions against charring are necessary<sup>8</sup> and the addition of antioxidants is desirable. Many of the recently developed mixed cellulose esters—formate acetate propionate butyrate mixed esters—are particularly suitable for application in this way, and the spate of patents covering the production of mixed esters<sup>9</sup> is evidence that at last some considerable attention is being devoted to modification of the cellulose component in the manner already indicated. The production of mixed esters, in which one at least of the esterifying agents is of the long-chain type, comparable with the fatty acids present in oils may perhaps represent an optimum film building unit (see *Ann. Repts.*, 1944, **29**, 318). L. W. Blanchard, jun.,

<sup>2</sup> *Off. Digest.*, 1944, No. 236, 288; B., 1944, II, 364.

<sup>3</sup> *Paint Oil Chem. Rev.*, 1944, **107**, No. 17, 9, 26; B., 1945, II, 61.

<sup>4</sup> *Paint Ind. Mag.*, 1944, **59**, 345; B., 1945, II, 116.

<sup>5</sup> *London Shellac Res. Bur.*, 1945, *Tech. Paper* 27; B., 1945, II, 188.

<sup>6</sup> B.P. 540,765; B., 1942, II, 66.

<sup>7</sup> B.P. 542,959; B., 1942, II, 203.

<sup>8</sup> U.S.P. 2,250,201; B., 1942, II, 288.

<sup>9</sup> Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,322,575; B., 1945, II, 214. Assrs. to Eastman Kodak Co., U.S.P. 2,316,866; B., 1945, II, 79. Assr. to Celanese Corp. of America, U.S.P. 2,192,277; B., 1945, II, 240. Brit. Celanese Ltd., B.P. 568,439; B., 1945, II, 214. Hercules Powder Co., B.P. 565,179; B., 1945, II, 79.



and C. L. Crane<sup>10</sup> claim the production of mixed esters containing dicarboxylic acid groupings. As J. K. Speicher<sup>2</sup> has pointed out, the nitrate has held the field largely through its ease of handling so far as formulation is concerned, whereas the acetate, which has some very desirable properties, has suffered through difficulties of compatibility. If these difficulties can be overcome by the partial replacement of the acetate by other organic acids, it is possible that the acetate may regain its place in the field of film-forming materials.

W. O. Baker,<sup>11</sup> in the course of an investigation of the X-ray diffraction characteristics of mixed cellulose esters, points out that only completely substituted esters yield ordered X-ray diffraction diagrams. Partial or mixed substitution leads to permanent local disorder in the polymer molecule. The addition of increasing proportions of plasticiser produces progressively greater and greater molecular disorder. X-Ray diagrams can indicate whether a plasticiser is a solvent or a non-solvent for a given polymer, characteristic diagrams being obtained in the case of two-phase systems. The number of plasticiser molecules rather than the molecular volume determines the extent of molecular disorder produced. Significant differences exist between the molecular arrangements of the cellulose and the starch triesters.

An extensive investigation of the properties of 49 plasticisers for cellulose nitrate has been reported by the Chicago Club.<sup>12</sup> In each case free films were prepared by means of the Dow film caster and tensile strength, elongation, and other properties were measured. It is not possible to summarise the mass of data presented within the confines of this report.

*cyclo*Hexyl phenyl ether, tribromodiphenyl ether, and chlorotetrabromodiphenyl ether are claimed to confer increased flexibility, toughness, and resistance to water, acids, and alkalis when employed as plasticisers with ethylcellulose according to S. L. Bass, T. A. Kauppi, and F. B. Smith.<sup>13</sup> L. P. Kyrides<sup>14</sup> claims the use of various substituted sulphon-*cyclo*hexylamides with both cellulose acetate and nitrate. The use of tetrahydrofuroates of furfuryl alcohol, glycols, and glycol ethers is the subject of a patent by J. B. Dickey and J. B. Normington.<sup>15</sup> In another patent by J. B. Dickey and J. G. McNally<sup>16</sup> the use of morpholine derivatives is claimed, but apparently these materials are liable to precipitation by any diluents present.

Aryloxyalkyl esters of cinnamic acid are suitable plasticisers for cellulose acetate and ethylcellulose according to G. H. Coleman and

<sup>10</sup> Assrs. to Eastman Kodak Co., U.S.P. 2,183,982; B., 1944, II, 354.

<sup>11</sup> *Ind. Eng. Chem.*, 1945, 37, 246; B., 1945, II, 186.

<sup>12</sup> *Convention-at-home-Daily, Amer. Paint J.*, 1945, 30, No. 6A, 16d.

<sup>13</sup> Assrs. to Dow Chem. Co., U.S.P. 2,189,337-8; B., 1945, II, 190.

<sup>14</sup> Assr. to Monsanto Chem. Co., U.S.P. 2,180,281; B., 1944, II, 354.

<sup>15</sup> Assrs. to Eastman Kodak Co., U.S.P. 2,186,631; B., 1945, II, 79.

<sup>16</sup> Assr. to Dow Chem. Co., U.S.P. 2,246,974; B., 1942, II, 219.



B. C. Hadler,<sup>17</sup> whilst G. H. Coleman, L. E. Mills, and G. V. Moore<sup>18</sup> claim the use of xenyl aryloxyalkyl ethers.

N. R. Kamath and B. S. Gidvani<sup>5</sup> state that the lac-cellulose ether lacquers give quite satisfactory performance except for low flexibility and poor adhesion. These defects can be overcome by the use of sextol phthalate or tricresyl phosphate (10%). Such lacquers containing as little as 7½% of ethylcellulose when used as finishing wood lacquers are superior to lacquers based on dammar and cellulose nitrate.

The effect of ultra-violet radiation on films of cellulose esters has been the subject of investigations by T. S. Lawton, jun., and H. K. Nason.<sup>19</sup> The degradation of the acetate is much less than that of the nitrate, which suffers more rapid change, especially in the initial stages. The effect is considerably reduced by replacing air by nitrogen, whilst controls kept in the dark were only very slightly affected. Similarly, V. A. Karfunkel and D. A. Fedorov<sup>20</sup> find that acetate films exposed to the atmosphere deteriorate more rapidly in summer and in southern climes, with a simultaneous increase in iodine value. The change is correlated with a reduction in the viscosity of cellulose acetate in solution in acetone on storage under similar conditions. The change is most rapid in impure acetone but is not dependent on the amount of acetone employed. Phenol, when present to the extent of the tricresyl phosphate used, does not affect the results.<sup>21</sup>

Inhibition of the effects due to exposure to ultra-violet radiation by the incorporation of  $\beta$ -naphthyl salicylate to the extent of 15% in cellulose films is claimed by H. Dreyfus.<sup>22</sup> Fabrics which have been impregnated with an alcoholic solution of this same reagent are likewise protected.

The production of emulsions of the oil-in-water type by the gradual addition of water to polyvinyl-cellulose emulsions of the water-in-oil type until phase inversion occurs, after which the rate of addition of water may be rapidly increased, is claimed by R. R. Lyne, J. Munro, and Imperial Chemical Industries Ltd.<sup>23</sup> On the other hand, A. Dreyling and W. W. Lewers<sup>24</sup> propose the production of oil-in-water type emulsions directly by the use of two emulsifying agents, one to be of the polar or interfacial tension lowering type and the other consisting of glue or casein, the presence of monohydric alcohols being advantageous. Cellulose nitrate damped with water may be employed if it is first kneaded to an emulsion of the water-in-oil type with the addition of solvents, phase reversal occurring on the addition of the emulsifying agents.

<sup>17</sup> Assr. to Dow Chem. Co., U.S.P. 2,248,491; B., 1942, II, 254.

<sup>18</sup> Assr. to Eastman Kodak Co., U.S.P. 2,249,518; B., 1942, II, 261.

<sup>19</sup> *Ind. Eng. Chem.*, 1944, 36, 1128; B., 1945, II, 77.

<sup>20</sup> *J. Appl. Chem. Russ.*, 1940, 13, 1375; B., 1945, II, 13.

<sup>21</sup> *Ibid.*, 1384; B., 1945, II, 13.

<sup>22</sup> B.P. 563,287; B., 1945, II, 315.

<sup>23</sup> B.P. 565,925; B., 1945, II, 123.

<sup>24</sup> Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,190,705; B., 1945, II, 283.



The use of sulphonated butylphenols as a means of increasing the viscosity of methylcellulose coating compositions is the subject of patent claims by K. D. Bacon and G. K. Greminger<sup>25</sup> as also by the Atlas Powder Co.<sup>26</sup>

Carboxymethylcellulose, according to J. K. Speicher,<sup>2</sup> is now being manufactured by the Hercules Powder Co., and has the advantage that in the form of its sodium salt it yields a viscous solution in water at 1% concentration and is capable of being rendered insoluble by means of weak acids or converted into the insoluble aluminium or calcium salts; it does not gel on warming as does methylcellulose, and is a promising material for the production of lacquer emulsions. Emulsion lacquers containing up to 33% of water and 33% of solids have been produced in U.S.A. for several years past, thereby effecting a considerable saving of solvent.

The use of a filler composed of cellulose acetate in the form of a water paste to fill pores and depressions on rough or porous surfaces, prior to coating with a cellulose lacquer of the conventional type, is proposed by British Celanese Ltd.<sup>27</sup>

The incorporation of ammoniacal silver nitrate and similar reducible salts of gold, platinum, or copper into acetate lacquers, and subsequent reduction of the dried film with reducing agents so as to produce mirror-like metallic surfaces, capable of being polished, is the subject of a patent claim by E. Freund and F. Deutsch.<sup>28</sup> War-time developments and peace-time prospects of cellulose lacquers are the subject of reviews by G. N. Hill,<sup>29</sup> L. Roon,<sup>30</sup> and A. K. Ash.<sup>31</sup>

*Analysis.*—A systematic procedure for the identification of synthetic resins and cellulose derivatives has been put forward by T. P. G. Shaw,<sup>32</sup> which has the merit of facilitating qualitative identification without the elaborate preliminary treatment characteristic of most schemes of this type.

C. J. Malm, L. B. Genung, R. F. Williams, jun., and M. A. Pile<sup>33</sup> propose to estimate the total acyl grouping present in cellulose esters by means of a stagewise saponification with 0.5N-alkali, followed by back-titration, whereby the cellulose is precipitated in a finely-divided state so that it interferes to a smaller extent with the end-point.

S. N. Danilov<sup>34</sup> proposes methods for the estimation of the reducing

<sup>25</sup> Assrs. to Dow Chem. Co., U.S.P. 2,321,270; B., 1945, II, 178.

<sup>26</sup> B.P. 569,189; B., 1945, II, 240.

<sup>27</sup> B.P. 570,005; B., 1945, II, 323.

<sup>28</sup> Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,186,452; B., 1945, II, 137.

<sup>29</sup> *Paint Oil Chem. Rev.*, 1944, **107**, No. 24, 14; B., 1945, II, 145.

<sup>30</sup> *Paint Ind. Mag.*, 1944, **59**, 349; B., 1945, II, 116.

<sup>31</sup> *Convention-at-home-Daily, Amer. Paint J.*, 1944, **29**, No. 4c, Oct., 27; B., 1945, II, 30.

<sup>32</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 541; C., 1945, 29. See also *Paint Tech.*, 1945, **10**, 55.

<sup>33</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 501; C., 1945, 25.

<sup>34</sup> *Trans. All-Union Conf. on Anal. Chem.*, 1944, **3**, 204; C., 1945, 25.



power of cellulose, the degree of oxidation of oxycellulose, and the extent of xanthation of viscose.

The determination of plasticiser content by means of a vacuum technique employing Dowtherm heating, with an accuracy of about 0.3%, is claimed by B. S. Biggs and E. K. Erickson.<sup>35</sup>

<sup>35</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 93; C., 1944, 169.

## PIGMENTS AND PAINTS.

By L. J. BROOKS,

*The British Anti-Fouling Compositions & Paint Co., Ltd.*

IN a year of transition from war to peace it is hardly to be expected that there should be any unusual developments. The literature mainly reflects a mood of "stock-taking," of exposure tests, and a recapitulation of the service results of substitutes. Most of the war-time expedients were adopted with misgivings, under duress, and one hopes that they will soon be abandoned without regrets; few indeed have caused surprise by good behaviour and merited revaluation. The search for new sources of raw material has yielded some interesting results which may have more permanent value.

The continuity of research has been maintained along the general lines of attack laid down in recent years. It is mainly directed towards a streamlining of production, and the continued and increasing application of modern physical methods of investigation, viz., X-ray and electron diffraction methods, and absorption in the ultra-violet and infra-red, including application of the Raman effect. Special attention is given to the crystallographic characterisation and the analysis of size, shape, surface area, and relative number of particles; the identification of amorphous and acicular zinc oxide and the anatase-rutile conversion of titanium dioxide are familiar examples of these.

By far the most stimulating advance in paints has concerned anti-fouling compositions, which have been the subject of intensive research in this country and in America.

### PIGMENTS.

The phthalocyanines and their metallic derivatives continue to be subjects of much activity. Only a most cursory review of this protean series can be given here. Those requiring more detailed information will find the whole field of phthalocyanines, their history, chemistry, structure, uses, and future prospects, comprehensively reviewed by P. L. Gordon.<sup>1</sup> A brief but able summary of recent developments is

<sup>1</sup> *Amer. Paint J.*, 1945, **29**, No. 40, 62.



provided by A. H. Woodhead,<sup>2</sup> and reference may be made to other contributions of this writer to an excellent series on "Recent developments in mineral technology."<sup>3</sup> The main lines of modern research are concerned with the problems of producing red or reddish shades, and a blue with a higher red reflex than the typical copper derivative Monastral Fast Blue B. Attempts are also made to cheapen these otherwise expensive colours by catalytic vapour-phase processes, and to refine them and improve their dispersion properties. No red colours have been developed and the possibilities of producing them by nuclear substitution are now considered to be exhausted. Progress is mainly concerned with the production of new green pigments of a tetraphenyl and tetrapyridyl series and their copper derivatives; these are described by J. W. Haworth, I. M. Heilbron, D. H. Hey, R. Wilkinson, and E. F. Bradbrook.<sup>4</sup> New sulphur type dyes have been prepared by heating a mixture of the phthalocyaninesulphonyl chloride and a mercaptan.<sup>5</sup> Methods for purifying and improving the dispersibility of porphines include a process of dissolving the phthalocyanine in concentrated sulphuric acid, and "drowning" the solution with water or dilute sulphuric acid; the pigment is then said to be recovered in a soft and easily dispersed form.<sup>6</sup>

There are few notable developments to report in the field of older pigments, although A. H. Woodhead<sup>7</sup> reports an interesting new method developed by G. P. Lutschinski and V. F. Tschurilkina for making Paris green, which eliminates the waste products of the copper sulphate process, by direct reaction of a low-temperature copper oxide with arsenious oxide and acetic acid.

The extensive subject of the so-called iron blues, *i.e.*, Prussian blues, Chinese and Milori blues, the toning blues used in printing ink, and the various soluble blues used in laundry blueing, are comprehensively and critically reviewed by H. Holtzmann.<sup>8</sup> He discusses the constitution of these complex derivatives of a polynuclear "berlinic acid,"  $\text{HFe}^{\text{II}}(\text{CN})_6\text{Fe}^{\text{III}}$ , and has investigated the possibility of forming nickel and other metallic berlinates, with the practical object of improving the alkali-resistance of these materials. A large measure of success is claimed to have been achieved with the nickel complex, which showed good resistance to a solution of pH 9.4 and was only slowly decomposed by 2N-sodium carbonate solution.

H. C. Boyson<sup>9</sup> has prepared a green pigment from grass with distinctive heat-reflectance properties. It is claimed to reduce considerably the

<sup>2</sup> *Paint Manuf.*, 1945, 15, 192.

<sup>3</sup> *Ibid.*, 165, 291, 329.

<sup>4</sup> *J.C.S.*, 1945, 409; A., 1945, II, 332.

<sup>5</sup> Imperial Chemical Industries, B.P. 566,740; B., 1945, II, 105.

<sup>6</sup> Sherwin Williams Co., U.S.P. 2,367,519; *Chem. Abs.*, 1945, 3167.

<sup>7</sup> *Paint Manuf.*, 1946, 16, 165; *J. Appl. Chem. Russ.*, 1940, 13, 867; B., 1940, 736.

<sup>8</sup> *Ind. Eng. Chem.*, 1945, 37, 855; B., 1946, I, 19.

<sup>9</sup> *Oil & Col. Tr. J.*, 1945, 108, 734.



interior temperature of houses, store-sheds, buses, and cars exposed to sunlight. Only a brief account of an interesting process is permissible here, of which the essentials are the extraction of chlorophyll and the replacement of its magnesium component by copper to form a green copper lake by digestion with 25% hydrochloric acid and treatment with an alcoholic solution of copper acetate. A striking example is given of its heat-reflectant properties, in which the behaviour of two model cars is compared, one being treated with a Brunswick green paint and the other with a paint pigmented with the chlorophyll derivative; on exposure to direct sunlight, the former showed a rise of 110° F. and the latter only 79° F. In addition, its use in infra-red camouflage paint is also demonstrated.

C. C. Downie reviews the progress in the production of red lead<sup>10</sup> and of sublimed lead white,<sup>11</sup> which has resulted in a greatly improved uniformity of both products, and in the case of the latter, a brilliant whiteness comparable with that of the best zinc oxide. The chief improvement in both cases involves considerable simplification of the process and in particular a rigid control of the temperature conditions, thus eliminating much tedious washing, levigation, and drying. For the production of litharge and red lead, the lead is first atomised by a blast of steam and air under pressure, and the proportion of  $\text{PbO}$  and  $\text{Pb}_3\text{O}_4$  is governed by the temperature: 550° for litharge and 450—500° for red lead. A higher temperature differentiation of 700° for litharge and 400° for red lead completes the oxidation. An electrical system of control is used to record changes of resistance in the heated mass due to varying proportions of  $\text{PbO}$  and  $\text{Pb}_3\text{O}_4$ .

This report has so far been mainly concerned with blue and green pigments; there have been no corresponding developments in white pigments with the notable exception of titanium products, which continue to be the subject of intensive study. The trimorphic character of titanium dioxide has been investigated in a fundamental manner by F. Barblan, E. Brandenberger, and P. Niggli<sup>12</sup>; they show the temperature-dependence of the three forms, anatase, brookite, and rutile, and have demonstrated that at 800—1000° the conversion of anatase into rutile is "disordered," whereas the orthorhombic brookite is converted in an ordered manner at 700°, the corresponding planes of the two modifications remaining parallel during transformation, but at 800° the conversion is again disordered. A. W. Hixson and R. E. C. Frederickson<sup>13</sup> have made a fundamental contribution towards an elucidation of the hydrolysis of titanium solution in sulphuric acid, the most important reaction in the manufacture of titanium dioxide. Previous workers had observed but failed to explain certain non-stoichiometric peculiarities in the

<sup>10</sup> *Paint Manuf.*, 1945, 15, 51; B., 1945, II, 278.

<sup>11</sup> *Ibid.*, 167; B., 1945, II, 310.

<sup>12</sup> *Helv. Chim. Acta*, 1944, 27, 88; A., 1944, I, 120.

<sup>13</sup> *Ind. Eng. Chem.*, 1945, 37, 678; A., 1945, I, 280.



precipitation curves. Freshly prepared aqueous dispersions of titanyl sulphate were shown to consist essentially of an unstable basic compound possessing colloidal properties, and the abnormal precipitation was considered to be due to peptisation of the hydrolytic products.

A number of other contributions are concerned with the complex colloidal character of the titanium solution and the difficulty of determining the optimum conditions for nucleation. This has led to a variety of patents which claim to effect efficient hydrolysis, chiefly by controlling the pH of the solution<sup>14</sup> and the rate and manner of adding the nucleating agent and diluent solution.<sup>15</sup> Most of these suggestions are of a semi-empirical character, but one interesting advance<sup>16</sup> is the use of alkali citrates for reversing the charge on a positively charged titanic acid gel, the resulting negatively charged sol of titanium dioxide providing the nuclei for hydrolysis.

A considerable variety of claims are made for improving the properties of titanium dioxide, especially chalk-resistance and durability, by controlling the anatase-rutile conversion and/or coating the particles with mono-layers of other metal oxides, before or during calcination. The production of the rutile form is said to be ensured by adding a small percentage of compounds capable of forming a compound with the titanium dioxide in the sodium chloride lattice or phenacite crystallographic group.<sup>17</sup> Other suggestions include the addition of insoluble silicates of the periodic groups II and III, especially rare-earth oxides<sup>18</sup>; the same company claims improved stability, reflectance, and chalk-resistance by coating the pigment with a complex mixture of chromium oxide, zirconium oxide, silica, and alumina,<sup>19</sup> and another patent advocates the introduction of antimony, molybdenum, and tungsten oxides.<sup>20</sup>

Alternative methods of production include a process in which high-temperature calcination is eliminated<sup>21</sup> by heating a mixture of the anatase and rutile hydrolysates at 200—350° for about an hour under pressure with a 5% solution of hydrochloric acid; the product is filtered off, washed, and dried. The same company claims to prepare a soft and uniform anhydrous precipitate by heating titanium tetrachloride or sulphate in an autoclave at 350—450°.<sup>22</sup> An entirely different approach involves the ignition of titanium tetrachloride in oxygen. J. Heinen<sup>23</sup> describes a process in which the tetrachloride is first preheated with oxygen at 1000—1100°; the green flame issuing from the first chamber

<sup>14</sup> National Titanium Pigments, B.P. 566,499; B., 1945, II, 121.

<sup>15</sup> Canadian Industries Ltd., Can.P. 422,334; *Paint Var. Prod. Man.*, 1944, 24, 332.

<sup>16</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,369,262; *Chem. Abs.*, 1945, 3680.

<sup>17</sup> National Lead Co., U.S.P. 2,316,840—1; B., 1945, I, 23.

<sup>18</sup> *Idem*, U.S.P. 2,346,188; *Chem. Abs.*, 1944, 5094.

<sup>19</sup> *Idem*, U.S.P. 2,346,322; *Chem. Abs.*, 1944, 5094.

<sup>20</sup> *Idem*, U.S.P. 2,170,940; B., 1944, II, 84.

<sup>21</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,358,167; *Chem. Abs.*, 1945, 1552.

<sup>22</sup> *Idem*, U.S.P. 2,345,980; *Chem. Abs.*, 1944, 4817.

<sup>23</sup> U.S.P. 2,367,118; *Chem. Abs.*, 1945, 2892.



passes to a condensation or reaction chamber, cooled at  $750^{\circ}$ , from which a smoke of the titanium oxide and chlorine is formed; a white and voluminous pigment is said to be prepared by this method.

There are several patents for improving the general utility of titanium dioxide by the preparation of composite pigments, in which the oxide is compounded with various other pigments and extenders. One process<sup>24</sup> describes the co-precipitation of titanium dioxide with calcium or barium sulphate; on calcination in presence of 1% of zinc oxide added as a converting agent, a voluminous rutile pigment of good whiteness and chalk-resistance is said to be formed. By a similar process<sup>25</sup>  $\alpha$ -titanic acid heated with zinc oxide  $600$ — $975^{\circ}$  gives, according to the conditions of calcination,  $\text{ZnTiO}_3$  of ilmenite structure or cubic crystals of  $\text{Zn}_2\text{TiO}_4$ , which may also be of spinel structure.

A number of metallic titanates of lead, zinc, and the alkaline-earth metals continue to receive attention, and in particular J. Rinse<sup>26</sup> reviews the uses and properties of lead titanate. As a result of numerous exposure tests, it is considered that the chief virtues of this pigment are its durability, and its property of protecting the media from photochemical decomposition; in these respects it is comparable with antimony-modified titanium dioxide, but offers no advantage over white lead in wood primers, and is definitely inferior to red lead in anticorrosive primers.

#### GENERAL.

The laborious and time-consuming outdoor exposure test is still perhaps the only satisfactory criterion of paint performance. An eminently practical study of the chalking of paints containing titanium pigments has been described by E. G. Rutter.<sup>27</sup> In particular the possibility of producing a durable and inexpensive hard-gloss paint has been examined. The materials for this investigation consisted of a number of carefully prepared and matured copal-rosin ester media of varying oil-lengths and different oils, viz., linseed, perilla, tung oil, and Dienol. These were incorporated in different proportions with mixtures of acicular zinc oxide, amorphous zinc oxide, anatase and rutile titanium dioxides, the general feature being varying proportions of titanium and zinc oxides. Some 300 panels were painted and exposed for two years at a site near the East Coast, and involved 15,000 observations. One series was applied to silver-steel panels, another to glass plates, and as a final experiment a house and bungalow were used for a general test on wood. The interesting theory is advanced that chalking is due to catalytic oxidation of the media by the pigment. It is suggested that the general faults of chalking, crazing, checking, and cracking are all varieties of the same phenomenon, probably conditioned by the size and shape of the

<sup>24</sup> National Lead Co., U.S.P. 2,369,468; *Chem. Abs.*, 1945, 5093.

<sup>25</sup> Sherwin Williams Co., U.S.P. 2,379,468; *Chem. Abs.*, 1945, 4240.

<sup>26</sup> *Chim. Peint.*, 1943, 6, 251.

<sup>27</sup> *J. Oil & Col. Chem. Assoc.*, 1945, 28, 187.



pigment agglomerates. The incidence of breakdown has been studied, and since it has been found to occur in successive stages, it has been related by a series of periodic analyses to the original distribution of solids and media in the film. It is considered that this distribution might have been initiated by a static charge induced on brushing. In conclusion, Rutter shows by a series of qualitative and quantitative graphs the excellent performance of a mixture of rutile titanium and accicular zinc oxide.

W. G. Varmoy<sup>28</sup> reports the general superiority, and in particular durability, of magnesium silicate as an extender in house paints as compared with calcium carbonate and calcium sulphate, although these are superior in colour retention, and calcium carbonate offers advantages in resistance to mildew.

The interaction of red lead in alkyd (phthalic) resin paints has been examined by A. J. Eickhoff, L. N. Kebrich, and J. G. Wills.<sup>29</sup> As is well-known, a similar soap-forming reaction produces beneficial results in other oleo-resinous media. Their investigation considered the degree of reactivity of red leads of varying true  $Pb_3O_4$  content, the degree of reaction between red lead and alkyd resin vehicle, and the solubility of the reaction products in the vehicle. As the success of the investigation depended on the efficiency of the analytical procedure, special attention was paid to a study of the available methods for determining phthalates in paint systems. They found that there was no reaction between true  $Pb_3O_4$  and alkyd resin, but only between free  $PbO$  and the vehicle. Red lead pigments containing more than 92% of  $Pb_3O_4$  do not react with alkyd vehicles to form lead phthalate, and even with those containing only 85% of  $Pb_3O_4$ , evidence of soap formation was not conclusive. They consider the present methods for determining phthalate content of the vehicle unsatisfactory, but sufficiently accurate for estimating the phthalate content of the extracted pigment. After long storage red lead-alkyd resin paint of 97% true red lead suffered no change in film flexibility. In this connexion also, the recent patent literature<sup>30</sup> includes a method for inactivating red lead by conversion of lead monoxide into carbonate by means of carbon dioxide.

P. Persoz<sup>31</sup> has made a detailed physical and mathematical study of the forces involved in a determination of the hardness of paint and varnish films, by means of a pendulum, the swing of which is governed by the penetration of the films at the point of pivot, and the internal friction of the substance studied. While poor agreement is acknowledged between the pendulum method and methods based on the use of pencils of graded hardness, it is submitted that the pendulum method is a more fundamental approach and may be used for the comparison of similar

<sup>28</sup> *Off. Digest*, 1945, No. 251, 558.

<sup>29</sup> *Ind. Eng. Chem.*, 1945, 37, 399; B., 1945, II, 247.

<sup>30</sup> Glidden Co., U.S.P. 2,182,567; B., 1945, II, 121.

<sup>31</sup> *Peint. Pig. Vernis*, 1945, 21, 322.



substances and the determination of drying time. As an important preliminary to a fundamental study of adhesion, Persoz<sup>32</sup> reviews the numerous and largely empirical instruments designed for the purpose of measuring adherence, and stresses the need for an exact terminology to distinguish the terms adhesion, adhesivity, and adherence; to this effect, a method for the measurement of adhesion in the exact sense is described.

E. Saffre<sup>33</sup> shows the necessity to distinguish physico-psychological and purely physical aspects of colour, in addition to the influence of reflectance and opacity in paint films. The essential principles of colorimetry and their application to the paint industry are competently reviewed. C. Zuber<sup>34</sup> makes an interesting contribution to the personal factors of colour. Few people see the same colour in quite the same way, and while appreciating the irreplaceable value of the human eye, its limitations must be recognised. The curious anomalies to which it may give rise are indicated and the means by which they may be detected described. In brief, the aim of the French contributors appear to be an attempt to rationalise our concepts of "why a paint sticks," and "why it is coloured," as a fundamental approach to a consistent and universal evaluation of "how strongly it adheres" and "how deeply it is tinted."

The effect of infra-red radiation on the rate of polymerisation of pigmented varnish films has received the attention of R. C. Ernst and J. I. Stevens,<sup>35</sup> who have investigated in a fundamental manner the life of such films in terms of reflectance, ageing, changes in distensibility, and the proportion of acetone-insoluble extract. The conclusions drawn are cautious rather than positive, and doubt is expressed not so much in the theory involved as in the instrumental means of demonstration. Tentative results indicated that the more infra-red is absorbed, i.e., the lower is the reflectance, the greater is the rigidity and the lower the distensibility of the film. Parabolic curves were obtained for tensile strength against reflectance. It is shown that the polymer content at constant reflectance changes materially during the life of the film, and finally that there was a critical stage in the life of the film where changes in physical properties were very great.

In the development of new materials for paints, P. L. Nichols, R. M. Hamilton, L. T. Smith, and E. Yanovsky<sup>36</sup> have examined the possibilities of the polyallyl ethers of starch and the simpler carbohydrates. In a paper of both academic and practical interest they give methods for preparing and determining the properties of these materials, in particular those of allylstarch. They indicate their importance in providing a variety of protective and decorative coatings for wood, glass, and metal. Waste products of the cereal industry and similar substances are shown

<sup>32</sup> *Peint. Pig. Vernis*, 1945, **21**, 162.

<sup>33</sup> *Ibid.*, 66.

<sup>34</sup> *Ibid.*, 130.

<sup>35</sup> *Amer. Paint J.*, 1945, **30**, 537.

<sup>36</sup> *Paint Ind. Mag.*, 1945, *Mar.*, 84.



by W. S. Penn<sup>37</sup> to form cheap and abundant raw materials for the preparation of furfuraldehyde and its derivatives. A rapid development of this highly reactive aldehyde is predicted; its cheapness, and the readiness with which it undergoes the familiar reactions of phenol and formaldehyde, may make it a formidable competitor of these materials. It is said to offer possibilities in the preparation of a solventless varnish and other specialities required by the electrical industry. It can also be used for functional coatings of an antiseptic character and may be modified to give thermo-setting plastics. It is also a valuable source of solvents for the paint industry.

The Chicago Production Club<sup>38</sup> have studied the properties and potentialities of organo-silicon compounds, viz., ethyl silicate, silica organosols, and silicone resins. They confirm and report favourably on their distinctive thermal properties, adhesion to glass, and the resistance of their films to chemical agencies. To a limited extent they are capable of contributing a degree of such properties to compatible organic compositions. The satisfactory stoving properties of ethylcellulose, polystyrenes, and polyacrylate media containing proportions of silicones are demonstrated, but no marked advantage was found in incorporating silicones with the more orthodox and familiar type of varnish resins. In addition, they show that a proportion of lead naphthenate reduces the stoving time and temperature of silicones, thus confirming the observations of H. A. Gardner and M. W. Westgate,<sup>39</sup> who have studied the catalytic curing of silicone resins, and have accelerated drying from one hour's stoving to 15 minutes' stoving at 250°, and who have also compared the effects of infra-red and ultra-violet radiation. They found that the disadvantage, associated with silicones, of lengthy stoving at high temperature could be overcome by the introduction of a suitable catalyst, preferably a lead compound, under the influence of radiant energy, an effect which they consider due to condensation or polymerisation, rather than to oxidation; in addition, they find that ultra-violet radiation, especially when lead is present, is very effective in removing tack.

The Technical Committee of the Cleveland Paint and Varnish Club<sup>40</sup> have made a study of antioxidants and anti-skinning agents, in which some 35 aromatic alcohols, amines, unsaturated aldehydes, phenols, etc. were added in small quantities to simple varnish systems of ester gum and linseed oil-alkyd media. They do not attempt to speculate on the mechanism of the antioxidant effect, but observe that resorcinol,  $\beta$ -naphthol, and a mixture of cresols (in that order) have pronounced and satisfactory effect on durability and weathering. In addition, butyrald-oxime and quinol were considered to be highly effective anti-skinning agents.

<sup>37</sup> *Paint Manuf.*, 1945, **15**, 151.

<sup>38</sup> *Off. Digest*, 1945, No. 250, 424.

<sup>39</sup> *Sci. Sect. Nat. Paint Var. Assoc.*, 1945, *Circ.* 705.

<sup>40</sup> *Amer. Paint J., Conv.-at-Home Daily*, 1945, **30**, No. 6B, 34.



P. L. Gordon, R. Aronowitz, and B. Cohen<sup>41</sup> have investigated the behaviour of vanadium linoleate, prepared from vanadium oxydichloride (liquid) and linseed oil fatty acids. They report that it is an effective drying agent, though less so than the corresponding soaps of cobalt and lead, but it is superior in its performance in hotter climates, where it maintains a more flexible film. They also indicate its use in the preparation of uniformly wrinkled films with tung oil and oiticica oil.

#### ANTIFOULING AND ANTICORROSIVE PAINTS.

The subject of antifouling paints continues to receive the notable attention it has attracted these last few years as a result of the general stimulus due to war-time naval requirements. The first detailed method for the evaluation of antifouling paints by determinations of leaching rate was contributed by B. H. Ketchum, J. D. Ferry, and A. C. Redfield.<sup>42</sup> It is emphasised, however, that it is intended to supplement and not to replace the practical criterion of sea-exposure. The method is based on the estimation of the amount of copper dissolved from unit area of the film in unit time, under standard conditions, in the test solution of seawater. The importance of an adequate volume of brine is stressed, otherwise the film would suffer premature inactivation due to the formation of insoluble products.

K. H. Pyefinch<sup>43</sup> provides a method of assessing antifouling efficiency in terms of the nature and extent of the observed fouling. More recently J. E. Harris and W. A. D. Forbes<sup>44</sup> have summarised the results of the leaching rate test for the evaluation of antifouling paints. (A general report on the antifouling work of the Marine Corrosion Sub-Committee, and a detailed description of the method, are in the press.) The main development is the provision of a method for determining leaching rate. Despite its limitations, it is claimed that it provides a convenient means of predicting performance and, in conjunction with a study of border diffusion effects, has led to the theory of the mechanism advanced. This postulates a very thin layer of toxic seawater at the surface of the film, corresponding to the dimensions of a laminar layer of fluid flow. A study was made of variations of the ratio of the components in the film, and the effect of grinding. It was shown, for example, that within limits, the leaching rate of copper was proportional to the amount of rosin in a rosin-oil medium; also that mercury oxide tends to decrease the release of copper, due, it is believed, to the formation of mercury soap. On the other hand, the release of mercury is favoured by the presence of zinc oxide. A mode of action for the release of copper was said to be effected through dissolution of the rosin or varnish matrix. A description is given of a rotor for use in durability tests, and finally notes are given on the method and results of raft exposure and large-scale

<sup>41</sup> *Amer. Paint J.*, 1945, 30, No. 3, 26.

<sup>42</sup> *Ind. Eng. Chem.*, 1945, 37, 456; C., 1945, 174.

<sup>43</sup> *Iron and Steel Inst.*, Jan., 1946; C., 1946, 144.

<sup>44</sup> Paper read Inst. Naval Architects, 12.4.46; *Paint Manuf.*, 1946, 16, No. 5, 151.



tests on ships, conducted, as it were, *in situ*, by periodic examination of the paint actually in service.

Anomalous inactivation of antifouling paints has been investigated by G. H. Young and G. W. Seagren.<sup>45</sup> They suggest that antifouling paints containing copper, and to a certain extent those containing cuprous oxide, may be inactivated if in too close proximity to the steel surface, by a process in which the soluble iron corrosion products precipitate the copper from its solution in sea-water in, or near, the interfacial region of the paint; in addition, a vicious circle may be created by the migration of copper ions to the steel surface, initiating an acceleration of corrosion. This view, however, was challenged by J. E. Harris,<sup>46</sup> who considered the electrochemical mechanism of corrosion and showed that cathodic alkali inhibited adequate leaching by reducing the solubility of the copper, in addition to mechanical blockage of the paint by rust formation.

Young and Seagren with J. C. Zahnen<sup>47</sup> have also studied the mechanism of accelerated corrosion under antifouling paint, and with M. H. Smith<sup>48</sup> have made a comparative study of the antifouling efficiency of DDT. The now familiar and distinctive toxicological properties of DDT have indeed attracted considerable attention. There have been several investigations into its use in both antifouling paints and interior finishes, but the influence of the media is still under investigation. Seagren, Young, and Smith have shown that DDT is very effective against barnacles but has no advantage in respect to other fouling organisms, and is unlikely to replace copper or mercury, thus confirming similar observations of R. E. Dimick,<sup>49</sup> who made preliminary studies of this material in antifouling compositions off the coast of Oregon.

H. Rabaté<sup>50</sup> reviews the toxicity of barium compounds in the paint industry, and in particular their use in fungicides and antifouling paints. The Ba<sup>++</sup> ion is toxic in varying degrees depending on the solubility of the compound. The application of cyanide compounds as a means of protection against corrosion is also discussed by the same author.<sup>51</sup> Their utility in underwater paints is well known, notably in the form of copper thiocyanate, and, in addition, the cyanides, ferrocyanides, and cyanamides of the alkali metals are said to provide good anticorrosive paints, especially for the protection of steel and ferrous alloys. H. Maseille<sup>52</sup> deals particularly with the electrochemical mechanism of corrosion. The small potential difference necessary to decompose sea-water is considered, and the ease with which this may be increased by the presence of such different metals as iron, copper, and bronze is indicated. The deleterious effect

<sup>45</sup> *Nature*, 1945, **155**, 715; cf. B., 1945, II, 278.

<sup>46</sup> *Ibid.*, **156**, 206; B., 1946, II, 214.

<sup>47</sup> *Ind. Eng. Chem.*, 1945, **35**, 461; B., 1945, II, 278.

<sup>48</sup> *Science*, 1945, **102**, 425.

<sup>49</sup> *Ibid.*, 10.

<sup>50</sup> *Peint. Pig. Vernis*, 1945, **21**, 152.

<sup>51</sup> *Ibid.*, 264.

<sup>52</sup> *Ibid.*, 290.



of stray currents of all types is described, and the need for efficient insulations of ships' electrical systems is emphasised. It is pointed out that the problem of providing a suitable paint might be relatively easy if it were not complicated by the necessity to provide quick-drying coats. The heterogeneity of modern welding steel renders it more difficult to protect and Mascille stresses the need to focus attention on the production of a homogeneous steel in order to eliminate at least one source of galvanic activity. Experience in the French naval yards has shown the definite superiority of brushing, as compared with spraying, which should not be resorted to except in emergency. In conclusion, Mascille revives the somewhat neglected subject of bacterial attack on organic films, and is of the opinion that, together with the nascent oxygen liberated by certain small green algæ, it makes a further contribution to purely chemical and electrochemical sources of attack.

The use of sparingly soluble chromates is now an accepted practice in the formulation of anticorrosive primers. W. G. Huckel and H. S. Davidson,<sup>53</sup> at the instance of the Detroit Production Club, undertook to investigate the use of zinc chromate and its modifications as inhibitors of corrosion. They emphasise the importance of comparable film thickness in this type of work and express a preference for the dip method of application. They show by exposure tests that the war-time expedient of using "chromatised" pigments was not justified, and reported severe failure as compared with zinc chromate. Tidal exposure tests on compositions prepared with zinc tetroxychromate in synthetic media did not justify the claims made for this material, although its performance in heat-bodied oil primers was satisfactory. On the other hand, a simple mixture of zinc oxide and zinc chromate was better than the synthetically compounded zinc tetroxychromate. They showed that the solubility of barium chromate is insufficient to maintain a "chromate reservoir" in films permeated by water; it would appear therefore that the success of conventional zinc chromate depends largely on its solubility completing the optimum conditions required in this connexion.

On the more practical aspects of the painting of ships H. H. Nelson<sup>54</sup> discusses the problem of correlating formulation with service conditions. It is conceded that better formulation can be devised by a carefully planned panel exposure programme, but the extravagant faith of some paint technologists in purely laboratory tests is deprecated. It is emphasised that the whole cycle of performance depends more than anything else on the conditions under which the paint was applied. In agreement with Mascille (*loc cit.*), the opinion is expressed that a closer co-ordination between the paint chemist and the personnel concerned in the preparation of the ship from the slips to the dry-dock would produce valuable results. It is considered that a power-driven wire brush is the best means of removing paint and rust, and of ensuring that the

<sup>53</sup> *Paint Ind. Mag.*, 1945, 60, No. 6, 190.

<sup>54</sup> *Sci. Sect. Nat. Paint & Var. Assoc.*, 1945, Circ. 710.



newly applied paint has at least a clean start. The U.S. Navy's experience with various functional types of paint is summarised, *e.g.*, fire-retarding, camouflage, potable water-tank coatings, deck paints, and anti-humidity paints. These have shown, under severe war-time conditions, the value of antimony oxide in an alkyd binder for the fire paints, the distinctive non-reflectant properties of a mixture of titanium oxide, zinc oxide, lampblack, and magnesium silicate in an alkyd medium, and the success of a zinc dust formulation for use in water tanks, provided the original steel is clean. A preference is expressed for the omission of zinc chromate and the use of a short-oil phenolic for Boot-top, although the general anticorrosive properties of the former are fully justified by experience on other parts of the ship.

#### ANALYSIS.

G. Zeidler and H. V. Szalatnay<sup>55</sup> submit a method for the general treatment of inorganic poisons in antifouling paints. It consists in a preliminary separation of the solids and liquids by centrifuge; mercury is then determined as the sulphide or by the formation of a mercury-gold alloy; arsenic is volatilised and determined as the chloride, and copper either colorimetrically as the cuprammonium complex, or iodometrically using sodium thiosulphate.

E. L. Bailes and M. G. Payne<sup>56</sup> describe a colorimetric estimation of DDT, which is an application of the Friedel-Crafts reaction, by means of which the white or colourless  $\alpha\alpha\alpha$ -trichloro- $\beta\beta$ -di-(*p*-chlorophenyl)ethane (the main constituent of DDT) is converted into an orange-green fluorescent compound.

I. Baker and G. Martin<sup>57</sup> provide a rapid method for the determination of alumina in titanium pigments. The sample is fused with pure sodium hydroxide in a nickel crucible, leached out in cold water, and filtered after a period of gentle boiling. A preliminary precipitation is effected by acidifying and neutralising with ammonia (and ammonium chloride); this precipitate is again adjusted and the solution oxidised with hydrogen peroxide; the aluminium is now precipitated as the oxine complex with 8-hydroxyquinoline. This is then followed by the bromate-bromide volumetric procedure, in which the complex is converted quantitatively into 5:7-dibromo-8-hydroxyquinoline.

C. H. R. Gentry and L. G. Sherrington<sup>58</sup> describe a rapid and precise method for both the gravimetric and volumetric estimation of mercury. The method is based on the insolubility of mercuric iodate in a 1% solution of nitric acid containing excess of iodic acid. The mercuric iodate is weighed as such, or decomposed by potassium iodide and concentrated hydrochloric acid, and the solution is then titrated with sodium thiosulphate using a starch indicator.

<sup>55</sup> *Chim. Peint.*, 1944, 7, No. 3—4, 30.

<sup>56</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 438; C., 1945, 269.

<sup>57</sup> *Ibid.*, 488; C., 1946, 5.

<sup>58</sup> *Analyst*, 1945, 70, 419; C., 1946, 4.



G. H. Osborn<sup>59</sup> gives a rapid and simple method for the determination of calcium in the presence of strontium and barium, which appears to be a distinct improvement on the older method based on the preferential solubility of calcium nitrate in ether-alcohol. It depends on the preliminary conversion of these elements into their sulphates, which are then easily and completely soluble in boiling perchloric acid; the solution of alkaline-earth perchlorates is evaporated to dryness, diluted with water, and on the addition of a little sulphuric acid barium sulphate is quantitatively precipitated; the strontium sulphate is precipitated later with stirring, and the calcium sulphate not at all, but is then easily estimated as oxalate in the filtrate. The method achieves a separation of calcium and barium and a separation of calcium and strontium for small amounts of either in the presence of the other.

R. J. Carter and L. Williamson<sup>60</sup> make a further contribution to the recent revival of interest in Karl Fischer's method of estimating small quantities of water by titrating the residual effect of water after its reaction with excess of solution of iodine and sulphur dioxide in methanol and pyridine. The reaction is not stoichiometric but may be standardised empirically. The authors have applied the method to water in resinous solutions, and appear to have reduced it to a simple routine operation, applicable to a wide range of coloured materials. This permits direct titration in a simple apparatus in which the end-point is recorded by the change of current registered on a galvanometer.

W. R. Schoeller and H. Holness<sup>61</sup> have recently made important contributions to the analytical chemistry of minerals and alloys by means of the tannin technique. Its chief application is to the metals of groups IV and V of the periodic system which under certain conditions of acidity form clear colloidal suspensions of their hydroxides; on the addition of tannin (a negative colloid) the metallic suspensions are neutralised and yield adsorption complexes by reciprocal flocculation. The method is of interest in providing a very convenient and accurate means of separating and estimating titanium dioxide. The titanium may be determined in either chloride or oxalate solution; the chloride method is mainly of interest in the separation of titanium from zirconium but the oxalate method<sup>62</sup> is of more general application. The method consists in gently fusing a small quantity of the solid containing titanium with a piece of acid potassium sulphate by rotating it in a small silica crucible until it melts without copious fuming. The clear melt is cooled and extracted with a hot saturated solution of ammonium oxalate. This is filtered if necessary and the acidity of the filtrate carefully adjusted; a solution of B.P. tannin is added near the boiling point. The bulky

<sup>59</sup> *Analyst*, 1945, 70, 207; C., 1945, 224.

<sup>60</sup> *Ibid.*, 369; C., 1946, 56.

<sup>61</sup> *Ibid.*, 319; C., 1945, 226.

<sup>62</sup> Schoeller and Powell, "The Analysis of Minerals and Ores of the Rarer Elements," 1940, 91 and 97.



orange precipitate is carefully washed with a dilute ammonium chloride solution and is then ignited and weighed as pure  $\text{TiO}_2$ .

I. M. Bernstein<sup>63</sup> describes a simple microscopic technique for the identification of ultramarine-blue and also cobalt-blues and violets in complex pigment mixtures. The method consists in ashing a small specimen of the ink or paint direct onto a microscopic slide, when the heat-resistant ultramarine may be identified in contrast with the lighter coloured ash of decomposed Prussian-blue.

Instrumental methods continue to be applied with varying success. H. P. Rooksby<sup>64</sup> uses the X-ray powder method for the determination of small amounts of zinc oxide in zinc sulphide, but acknowledges that the lower limits of an analysis by this method are not perhaps as good as they might be; he suggests that photometric means may improve it. J. S. Buhler<sup>65</sup> advocates the use of an X-ray spectrometer in conjunction with a Geiger counter as an accurate method for the rapid analysis of paint materials.

<sup>63</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 262; C., 1945, 244.

<sup>64</sup> *Analyst*, 1945, **17**, 166; C., 1945, 155.

<sup>65</sup> *Paint Oil Chem. Rev.*, 1945, **13**, No. 108, 10.



# RUBBER.

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AVAILABLE statistics of the crude rubber situation come solely from America at present, and the picture is substantially the same as that given in last year's Annual Report.

## PRODUCTION OF SYNTHETIC RUBBER IN THE U.S.A.,<sup>1</sup> LONG TONS.

Year.	GR-S.	GR-L.	GR-M.	GR-A.	Total.
1944 .. .. .	668,840	18,890	47,302	2060	737,092
1945, estimated ..	881,000	53,000	55,000	0	989,000

	Natural Rubber,		Synthetic,
	Imports.	Stocks.	Stocks.
1944 .. .. .	109,000	99,000	145,000
1945, estimated..	123,000	65,000	189,000

The Rubber Study Group,<sup>2</sup> composed of representatives of the Governments of the Netherlands, the U.K., and the U.S.A., established in September, 1944, held its first conference in Washington in January, 1945, and while emphasising the great uncertainty in rubber production and consumption in the next few years, concluded that by 1948-49 there will be a total output of 2,833,000 tons per year (1,500,000 tons natural), with a probable consumption of no more than 1,500,000 tons per year. Very difficult problems may arise, therefore, if the market is swamped.

The news trickling out of Malaya<sup>3</sup> since the reoccupation is of such a conflicting nature, ranging from stories of extensive damage to negligible damage on the rubber estates, that it is yet impossible to decide how soon the planting areas will be rehabilitated. The stories include reports of considerable stocks of rubber, *e.g.*, 12,000 tons in Penang, 33,000 in Johore, 35,000 in Java, 115,000 in Indo-China, and the first ship left Singapore on September 18th with 500 tons of rubber in its cargo.

Steps have been taken in the intricate problem of rehabilitating Malayan rubber. The British Military Administration has appointed a Rubber and Produce Buying Unit to be sole owner of rubber in Malaya, and the Rubber Growers' Association has formed a Malayan Rubber Estate Owners' Company, without shares, to unite all owners in the orderly sharing out of the very scanty supplies of personnel and materials.<sup>4</sup> Similar arrangements have been made in Borneo, but the Netherlands East Indies have remained in a state of confusion.

<sup>1</sup> U.S. War Production Board, Rubber Bureau, 1944 Year End Report, 1945.

<sup>2</sup> *India Rubber J.*, 1945, 108, 119.

<sup>3</sup> See, *e.g.*, *Financial Times*, 1945, Sept. 17, Oct. 15; *Times*, 1945, Sept. 14, 19, 22, Oct. 5.

<sup>4</sup> *Financial Times*, 1945, July 23, Sept. 19.



## LATEX.

Determination of the dry rubber content of latices is at best an arbitrary process, and where coagulation by acids is irregular or impossible the standard methods are inapplicable. P. Compagnon and J. le Conte<sup>5</sup> have proposed a neat general micro-method; a few drops of the latex are placed between two microscope slides, alcohol is infiltrated to effect coagulation, and the thin film of coagulum obtained is washed with hot water, dried, and weighed. Results do not deviate from the mean by more than  $\pm 1\%$ .

Bulk coagulation of latex by electrical current was patented by Cockerill as long ago as 1907 but proved uneconomical. There is a new South African patent application,<sup>6</sup> using a.c., 220 volts, 50 cycles, to flocculate the latex, which seems to be making some progress in the Belgian Congo, Nigeria, and the Gold Coast.

Search has been made for further plant extracts, analogous to several developed during the war, for creaming latex and A. K. M. Pillai<sup>7</sup> reports that the gummy aqueous extract from the seed cover of *Trigonella foenum-græcum* is even more efficient than sodium alginate, yielding creams of 58—63% dry rubber content in 6—96 hours. The creams keep well for months.

A somewhat unusual method<sup>8</sup> of purifying latex, especial high-protein centrifuge skim, consists in adding to the latex an ethylenepolyamine of 3 or more amino-groups and an alkyl sulphate of 10—18 carbon atoms, when adjustment of the pH to a value greater than 5 flocculates the latex. The flocks are easily washed with water and may then be redispersed by adding alkali, or may be dried to pure solid rubber. Quebrachitol<sup>9</sup> has been separated from latex and isolated by precipitation with lime at a raised temperature.

The particularly stable state of latex at pH 9.8—10.0 pointed out last year now almost invariably appears in patents for preserving latex and is used for the latest proposed stabilisers,<sup>10</sup>  $\alpha$ -aminoethyl alcohol and zincates.

The war drive in connexion with wild rubbers has dwindled almost to nothing and the doubled output will no doubt dwindle also, but investigations of some of the latices of wild rubbers have been unusually numerous. The Indian project to cultivate *Cryptostegia grandiflora* has resulted in a wide search for coagulants.<sup>11</sup> As little as 0.1% of almost any acid, including carbon dioxide from the mouth, gives a coagulum of good strength easily sheeted. Alkalis and organic bases yield tacky spongy

<sup>5</sup> *Rev. Gén. Caoutchouc*, 1944, 21, 102.

<sup>6</sup> E. L. Gericke and P. Torr; see *India Rubber J.*, 1944, 107, 577.

<sup>7</sup> *Current Sci.*, 1944, 13, 322; B., 1945, II, 194.

<sup>8</sup> United States Rubber Co., B.P. 567,151; B., 1945, II, 157.

<sup>9</sup> *Idem*, U.S.P. 2,378,141.

<sup>10</sup> B. F. Goodrich Co., U.S.P. 2,318,813; B., 1945, II, 125; U.S.P. 2,361,070.

<sup>11</sup> R. H. Siddiqui, S. A. Warsi, and V. V. K. Sastri, *J. Indian Chem. Soc.*, 1944, 21, 191; B., 1945, II, 123.



coagula of low strength, but these faults can be eliminated by a 15-minute dip of the coagulum in weak acid. Small quantities of a variety of salts give good coagulation; e.g., 1 part of common salt, calcium chloride, or alum will coagulate 21,500 parts of latex of 2—7% dry rubber content; 6 volumes of boiling fresh water will serve the same purpose. Auto-coagulation due to bacterial action takes place in a few days at 30° C. Similar investigations have been made on mangabeira latex by R. D. de G. Paula.<sup>12</sup> Beating or shaking is the method preferred for this latex, yielding a good light-brown rubber, whereas chemical coagulation with acetone, alum, or alcohol is slower and the rubber is of inferior elasticity and ageing-resistance. Confirmatory observations have been reported by L. R. Guimarães and J. M. Chaves,<sup>12</sup> who consider that the stabilising agent in the latex is a protein.

*Funtumia* latex from the Gold Coast has set tappers and processors a problem in detecting adulteration with water during the war drive. On the Far Eastern estates it is customary to use a hydrometer graduated to give a direct reading of rubber content, the results being sufficiently accurate for factory work. M. Greenwood<sup>13</sup> has shown that this method is unreliable on small samples of *Funtumia*, though it gives a rough approximation on samples of 4 gallons or larger. He proposes as a substitute to use the close correlation between relative viscosity and dry rubber content and describes a simple viscometer suitable for field work.

#### RAW RUBBER.

The breakdown of chemical bonds in the long chains of unvulcanised rubber is of such great practical importance in relation both to the ageing of rubber products and to the plasticising of rubber in works processing that it is not surprising the subject rarely rests. In the year under review almost every line of approach to the problem has been resumed. E. H. Farmer<sup>14</sup> has reviewed the oxidative breakdown, which is summarised as due to the formation of peroxides or peroxido-radicals, stable or unstable, and liable to form cross-links at some points in the chains while severing them at other points. Peroxido-links may form from chain to chain, or between different points of one chain, independently of links formed by secondary breakdown of peroxides at external bonds. The picture conveyed is of a medley of different operations distributed by chance at random points in the chains, and this agrees well with the wide variability in "average ageing results" obtained in practice. When the breakdown is carried to a state of appreciable oxidation, as in "Rubbone" or nitrite-rubber, very little peroxidic oxygen remains<sup>15</sup> and the hydroxyl content is high. In nitrite-rubber

<sup>12</sup> *Anais Assoc. Quim. Brasil*, 1944, 3, 109; B., 1945, II, 34. *Ibid.*, 95; B., 1945, II, 33.

<sup>13</sup> *India Rubber J.*, 1945, 108, 533, 537, 564, 599; C., 1945, 174.

<sup>14</sup> *Preprint, I.R.I. Symposium, Birmingham, May, 1945.* See also D. F. Twiss, *India Rubber J.*, 1945, 108, 731; 109, 14; B., 1945, II, 284.

<sup>15</sup> R. F. Naylor, *Trans. Inst. Rubber Ind.*, 1944, 20, 45; B., 1944, II, 374.



some 60% of the oxygen is not detectable as peroxidic, hydroxylic, carboxylic, or carbonylic, and is probably found in cross-links.

Photochemical breakdown<sup>16</sup> of a highly purified fraction of caoutchouc, degassed, and at a pressure of  $10^{-6}$  mm., occurs so rapidly that gas formation is obtained immediately irradiation with a mercury arc is begun, though the actual formation of gas,  $10^{-7}$  g.-mol. per hour, is very small.

Thermal breakdown, as discussed by J. L. Bolland and W. J. C. Orr,<sup>17</sup> is apparently not such a random affair as oxidative breakdown. The chains separate at the bonds of lowest stability. Theoretically these occur at the junctions of the isoprene links, and it is an observed fact that in the temperature range 220—270°, the predominant volatile products are isoprene and dipentene.

The practical breakdown which forms an early stage of nearly all rubber processing, variously termed mastication, softening, plasticisation, peptisation, and depolymerisation, has received a new name from W. B. Warden,<sup>18</sup> namely, "fluidification," with a view to avoiding all theoretical inferences. He gives data on the satisfactory results obtained with stearyl peroxide as a "fluidifying" reagent when special care was taken to eliminate all traces of the reagent before completion of processing. The essential oxygen factor in the mastication process has been used to negative the widely held view that sulphur has an antioxidant effect in rubber<sup>19</sup>; the addition of sulphur to a mixing at the beginning or end of the mastication process apparently has no effect on the results. A. Haehl and P. van den Weghe have previously shown that the roll "friction" ratio has no special influence on the purely mechanical breakdown of rubber, but they have now further shown<sup>20</sup> that in compounding rubber, over a friction range from 1 : 1 to 1 : 2.5 the optimum stocks are obtained in the 1 : 1.5 to 1 : 2 region. With lower ratios dispersion is bad and with higher ratios the rubber is degraded and accident risks are serious.

As in the case of the wild rubber latices, the wild rubbers themselves have been extensively investigated. Correct moisture conditions and forced aëration have been shown to give an improved guayule rubber<sup>21</sup> of reduced resin content and better tensile strength; treatment of crude guayule with 5% caustic soda solution in steam at 150° for 8 hours has been claimed to improve tear-resistance, flex-resistance, resilience, and general "nerve," with definitely superior road service in tyres.<sup>22</sup> A detailed comparison of latex guayule, deresinated guayule, and retted,

<sup>16</sup> L. Bateman, *Preprint, I.R.I. Symposium, Birmingham, May, 1945.*

<sup>17</sup> *Ibid.*

<sup>18</sup> *India Rubber World*, 1944, **111**, 309, 317; 1945, **111**, 432; B., 1945, II, 195.

<sup>19</sup> Res. Assoc. Brit. Rubber Manufs., *J. Rubber Res.*, 1944, **13**, 166; B., 1945, II, 64.

<sup>20</sup> *Rev. Gén. Caoutchouc*, 1944, **21**, 23.

<sup>21</sup> J. W. White, jun., J. Naghski, P. J. Allen, S. R. Hoover, and J. J. Willaman, *India Rubber World*, 1945, **111**, 570; B., 1945, II, 194.

<sup>22</sup> Wingfoot Corp., B.P. 568,067; B., 1945, II, 230.



old, Texas, young, and Mexican grades of guayule in a carbon black stock<sup>23</sup> has put the samples in the foregoing order of decreasing merit; there is little to choose between the first two though both are inferior to *Hevea* smoked sheet. Retted guayule is better than the following types only in tensile strength.

*Ficus maroma* rubber, not traced as having been examined previously, has been shown by G. Dalma<sup>24</sup> to contain 75% of resins, 3% of proteins, and 0.5% of mineral matter, with a strength after deresinification only 60% of that of *Hevea*. For use during the war scarcity, golden-rod rubber has been extracted in the U.S.A. as a benzene solution, and this has suggested compounding the solution rather than the sticky rubber itself.<sup>25</sup> In practice it has proved effective to add sulphur, accelerator, and zinc stearate, followed by "setting" the dissolved mixture by limited heat-treatment, finally adding any other ingredients required to the then easily handled recovered solute. Vulcanisates obtained by this method have shown tensile strengths as much as 2000 lb. per sq. in. above normal results. Further to the work on *Cryptostegia* latex already noted, rubbers obtained by 23 methods of coagulation have been examined<sup>26</sup> and it can be said broadly that the quality did not vary appreciably with the coagulant.

#### *Vulcanisation and Accelerators.*

The important method of infra-red absorption spectra has been applied to vulcanisation studies by N. Sheppard and G. B. B. M. Sutherland.<sup>27</sup> Though the results in this field are too meagre for extensive conclusions, it seems to be established that the ethylenic double bonds persist appreciably after vulcanisation, even vulcanisation to a high degree. Two new absorption bands appear, one of which is probably associated with C-S links; the band due to the accelerator in the unvulcanised stock disappears. Incipient vulcanisation or "scorching" is generally measured by the changes in plasticity or solubility in benzene of the stock. These methods have been compared<sup>28</sup> and found practically identical, though the latter is the less sensitive and carbon black in the stock interferes. Attempts to use the time required for a solution to gel on heating were a failure. In an attempt to explain why heavily milled rubber is less prone to scorching than normally milled rubber, S. Buchan<sup>29</sup> has examined numerous factors that might affect vulcanisation. Paraffin wax and acidic softeners retard scorching, but the most

<sup>23</sup> F. E. Clark and W. F. L. Place, *India Rubber World*, 1945, 112, 67; B., 1945, II, 228.

<sup>24</sup> *Ind. y Quim.*, 1945, 7, 103; B., 1945, II, 228.

<sup>25</sup> F. L. McKennon and J. R. Lindquist, *Rubber Age* [N.Y.], 1944, 56, 289; B., 1945, II, 124.

<sup>26</sup> R. H. Siddiqui and M. L. Mathur, *J. Indian Chem. Soc.*, 1944, 21, 215; B., 1945, II, 123.

<sup>27</sup> *Trans. Faraday Soc.*, 1945, 41, 261; A., 1945, I, 184.

<sup>28</sup> J. F. Morley, J. R. Scott, and W. H. Willott, *J. Rubber Res.*, 1944, 13, 168; C., 1945, 30.

<sup>29</sup> *Trans. Inst. Rubber Ind.*, 1944, 20, 93; B., 1945, II, 64.



probable explanation is found in atomic oxygen; as obtained by treating a rubber solution with hydrogen peroxide this agent appreciably retards "set-up," while molecular oxygen has no effect. Attempts to simulate the atomic oxygen effect with copper powder failed to give any indication of the copper acting as an oxygen carrier.

H. P. Stevens<sup>30</sup> has carried out extensive investigation of photovulcanisation, exposing rubber *in vacuo* or in an inert gas to sunlight and to ultra-violet radiation. Photovulcanising agents, usually photogelling agents for rubber solutions, when dusted on the rubber surface greatly enhance the reaction; they include aldehydes, ketones, quinones, and sulphur. Molecular oxygen is a powerful photogelling agent but is not an effective photovulcanising agent. Sunlight is regarded as more powerful than an ultra-violet lamp, but it should be realised that the degree of vulcanisation under consideration in these experiments is not more than that of an accelerated stock brought to about 0.3% of combined sulphur in a normal thermal vulcanisation. Since photovulcanisation can occur in the absence of any enhancing agent, it is pointed out that it is necessary to add to the "sulphur bridge" theory of vulcanisation the possibility of direct C-C links between adjacent chains.

Technique in practical vulcanisation changes only slowly with the years, but this is not always evidence of indifference to progress. The war, for example, created a scarcity in French chalk for embedding articles to be vulcanised in open steam (the chalk supplies a chemically-inert mechanical support to the soft rubber and has to cope with condensation and iron rust). A questionnaire to the industry<sup>31</sup> has revealed that china clays, whiting, light magnesium carbonate, slate powder, and asbestine all serve the same functions moderately well in general, but all fail in the most exacting cases. There has developed a strong trend in favour of high-frequency dielectric heating for vulcanisation in suitable cases, though the inability to use this method for moulded goods is a serious limitation, and attention may be drawn to a detailed survey of the subject.<sup>32</sup>

For some years comment has been made in these Reports on the striving to obtain improved derivatives of thiolthiazole accelerators of vulcanisation. This tendency has resulted in many complex compounds, and although it seems to be waning, the most recent proposals are as complex as any—reaction products of the thiolthiazole with cyclohexylamine and paraformaldehyde,<sup>33</sup> thiazyl cyanoethyl sulphides obtained by interaction of the thiolthiazole with acrylonitrile,<sup>34</sup> and products

<sup>30</sup> *India Rubber J.*, 1945, **108**, 9, 12, 35, 65, 68, 91, 122, 124; B., 1945, II, 124.  
*J.S.C.I.*, 1945, **64**, 135; B., 1945, II, 228.

<sup>31</sup> T. R. Dawson, *J. Rubber Res.*, 1945, **14**, 8; B., 1945, II, 124.

<sup>32</sup> T. H. Messenger and D. V. Onslow, "Capacity Current Heating of Electrical Non-Conductors," *Brit. Elect. & Allied Ind. Res. Assoc., Tech. Rept. Y/16*, 1945.

<sup>33</sup> Monsanto Chem. Co., U.S.P. 2,360,449.

<sup>34</sup> Wingfoot Corp., B.P. 564,412; B., 1944, II, 348.



formed by treating ammonia with 2-chlorothiolbenzthiazole to substitute two or three of the H atoms in the ammonia.<sup>35</sup>

Interest seems to have been transferred from the foregoing group mainly to the corresponding hydrogenated compounds, the thiazolines. In addition to new syntheses of the parent 2-thiolthiazoline,<sup>36</sup> there has been a definite move towards new derivatives. The B. F. Goodrich Co.<sup>37</sup> have described interesting advantages in using 2-thiolthiazoline in the presence of a monocarboxylic acid and have gone on from this step to the use of a mixed zinc salt of the foregoing components. The active hydrogen in the SH group of the thiazoline has been transformed also into a variety of higher alkylamine radicals or into arylamine radicals, attached to the sulphur through a nitrogen atom in either case,<sup>38</sup> and attention has been given to esters of 2-thiolthiazoline, the 2:4-dinitrophenyl ester in particular, stress being put on the need to use a monocarboxylic acid such as lauric acid with these accelerators.<sup>39</sup>

Of what may be called new classes of accelerator, it is now rather difficult to be certain, but a group of thiocarbamyl sulphamines, described by the United States Rubber Co.,<sup>40</sup> may probably be so termed. Accelerators of high efficiency are found in the dimethyl, di-*n*-butyl, dibenzyl, cyclopentamethylene, and oxydiethylene members of the group.

#### *Raw Rubber Transformation Products.*

There is an interesting resemblance between two recent patents<sup>41</sup> for obtaining cyclised rubber. In the first rubber, aluminium hydrogen sulphate, sulphur, and phosphoric acid are heated together, and in the second rubber, alum, phosphorus pentoxide, and free sulphuric acid. Both products are claimed as particularly useful in bonding rubber to metals. The stabilisation of *cyclorubbers* has not been greatly stressed hitherto, but these derivatives are subject to photochemical darkening of colour and to loss of strength under the influence of heat. Additions<sup>42</sup> to the few stabilising agents already patented include a wide range of water-insoluble resins containing amino-nitrogen. Particular compounds in the first patent are  $\beta$ -di-*n*-butylaminoethyl methacrylate, polymethyl vinyl ketone hydrogenated in the presence of ammonia, and cyclohexanone-formaldehyde-methylamine, phenol-formaldehyde-thiourea, and cresol-formaldehyde-melamine condensation products; the other patents refer to condensation products of polyalkylenepolyamines with

<sup>35</sup> United States Rubber Co., U.S.P. 2,321,306; B., 1945, II, 196.

<sup>36</sup> *Idem*, U.S.P. 2,321,296; B., 1945, II, 172. E. I. Du Pont de Nemours & Co., U.S.P. 2,364,398-9.

<sup>37</sup> U.S.P. 2,358,717, 2,356,932-3.

<sup>38</sup> Firestone Tire & Rubber Co., U.S.P. 2,367,827. United States Rubber Co., U.S.P. 2,370,253.

<sup>39</sup> B. F. Goodrich Co., U.S.P. 2,363,598.

<sup>40</sup> U.S.P. 2,318,482; B., 1945, II, 196.

<sup>41</sup> Advisory Council for Sci. & Ind. Res., Ottawa, U.S.P. 2,311,656; B., 1944, II, 335. General Tire & Rubber Co., U.S.P. 2,379,939.

<sup>42</sup> E. I. Du Pont de Nemours & Co., B.P. 567,496; B., 1945, II, 197. Wingfoot Corp., B.P. 568,787; U.S.P. 2,371,736-7; B., 1945, II, 286.



aldehydes, and to amides of the polyamines with various carboxylic acids.

Interest in chlorinated rubber has been mainly in transformations of its physical form,<sup>43</sup> with reference to obtaining the material in dense chips or flakes by pressure-crushing wet fluffy products; or in cellular masses by partly filling moulds and heating at 300—350° F. until decomposition gas from the chloride expands the residue; or in aqueous emulsion using a glycol ester of a rosin acid as emulsifying agent. Stabilisation against heat, which has long been a serious problem with chlorinated rubber, received one new suggestion<sup>44</sup> for the use of small proportions of sodium carbonate in association with a diphenyl-, dinaphthyl-, or dichlorodiphenyl-thiourea.

Rubber hydrochloride has been prepared from waste vulcanised rubber<sup>45</sup> by digesting the scrap with a solvent such as toluene containing 5% of naphthalene at 130—170° to obtain the rubber in solution, followed by passing in dry hydrogen chloride at -10°. Although there is nothing to report this year on the stabilisation of rubber hydrochloride, much has been said on the subject in the past, and in general the stability of raw rubber transformation products leaves much to be desired. The rubber-phenol and rubber-naphthol products patented in 1940 as excellent adhesives must now be added to the unsatisfactory group, since it has been found necessary to protect their adhesive power and colour against deterioration<sup>46</sup>; the agents proposed are the same amino-nitrogen-containing resins summarised above in connexion with *cyclorubber*. These rubber-phenol condensates have been further condensed also with maleic anhydride,<sup>47</sup> but it is not clear whether this is a stabilising measure or to obtain other properties.

Some novel derivatives have been described by the Monsanto Chemical Co.<sup>48</sup> Pale crêpe is dissolved in an inert solvent such as carbon disulphide and heated with an arylphosphine halide; preferred halides include tolyl-, xylyl-, diphenyl-, and  $\alpha$ -naphthyl-dichlorophosphine. The products in suitable cases are tough, rubber-like bodies, but capable of having fillers dispersed in them much more easily than is untreated rubber; in other cases the products act as excellent softeners and plasticisers for rubber. Another novel class of derivatives<sup>49</sup> is water-miscible; it is obtained by heating an organic amine at its boiling point with rubber.

#### SYNTHETIC RUBBER-LIKE MATERIALS.

The flood of information on *ad hoc* studies of synthetic rubber continues with little or no intermission, much as indicated in last year's Annual

<sup>43</sup> Hercules Powder Co., U.S.P. 2,182,473; B., 1945, II, 36; U.S.P. 2,371,899. United States Rubber Co., U.S.P. 2,371,382.

<sup>44</sup> H. Fikentscher, U.S.P. 2,365,400.

<sup>45</sup> G. Frenkel, B.P. 567,236; B., 1945, II, 158.

<sup>46</sup> E. I. Du Pont de Nemours & Co., B.P. 567,364; B., 1945, II, 196.

<sup>47</sup> *Idem*, U.S.P. 2,364,158.

<sup>48</sup> B.P. 568,288; B., 1945, II, 253. U.S.P. 2,364,394, 2,367,264.

<sup>49</sup> M. Dennis Co., U.S.P. 2,364,186.



Report. While it represents an indispensable background of practical information, it does not amount to theoretical progress and is in general omitted from the following sketch of the position.

The grading and standardisation of the American Government rubbers have made substantial advances and there are now effective working specifications for GR-S, GR-S latices, GR-S-AC (the alum-coagulated type of GR-S), GR-I, and GR-M, all emanating from the Rubber Reserve Co.<sup>50</sup> Probably as a result of this narrowing of properties within known limits, determined by comparable methods of test, there have been few recent comparison investigations, and the only other topic of general application calling for mention seems to be that of reclaiming (a word tending to be replaced by "regenerating"). The important point in this field is to discover a method that gives good results for all synthetic rubbers, or at least for the group of butadiene co-polymers, otherwise the problem of sorting scrap will be insuperable. J. S. Plumb<sup>51</sup> has observed that peptising agents, *e.g.*, dihydroxyaryl sulphides, mercaptans, and hydrazines, have been found particularly effective for general use, and the first-named materials have been patented<sup>52</sup> both for the butadiene group and for GR-M. The Dunlop Rubber Co.<sup>53</sup> have patented a general method in which the comminuted rubber is worked between rolls with a softener, *e.g.*, pine oil, at a temperature below 60° and, after sheeting occurs, at 60—120°. The product can be moulded with the aid of heat and pressure without any additions, or will easily blend with new rubber. It retains some 75% of the durability of new rubber.

GR-M stands somewhat apart from the butadiene group in regard to reclaiming. Specific chemical reagents<sup>54</sup> proposed for improving the heat-milling reclaiming of this rubber include piperidinium acetate, sugars such as sucrose or glucose, and carboxylic acids, preferably oleic, oxalic, or lactic acid. The Dryden Rubber Co.<sup>55</sup> have indicated that an important detail in reclaiming GR-M is to remove most of the magnesia present by treatment with hot acid, and this may well be a factor in the efficiency of some of the reagents just noted.

The detail properties of the chief synthetic rubber reclaims are being subjected to examination<sup>56</sup> and it is possible to conclude that all of them are somewhat inferior to the corresponding new rubbers, but not markedly different from natural rubber reclaims. In the case of GR-S an increased

<sup>50</sup> In addition to the separate specifications as pamphlets, 1944-45, see *India Rubber World*, 1944, 110, 418; 1945, 111, 446, 700; 112, 199; B., 1944, II, 379; 1945, II, 195.

<sup>51</sup> *Ibid.*, 1945, 112, 307; B., 1945, II, 285.

<sup>52</sup> W. G. Kirby and L. E. Steinle, U.S.P. 2,359,122, 2,363,873.

<sup>53</sup> B.P. 564,514; B., 1944, II, 380.

<sup>54</sup> United States Rubber Co., B.P. 561,768, 563,753, 566,058; B., 1944, II, 366; 1945, II, 65, 158.

<sup>55</sup> U.S.P. 2,313,693; B., 1944, II, 380.

<sup>56</sup> E. B. Busenberg, *Rubber Age*, 1945, 57, 181; B., 1945, II, 285. R. L. Randall, *ibid.*, 1944, 56, 65; B., 1945, II, 64. F. L. Kilbourne, *India Rubber World*, 1945, 111, 687, 699; B., 1945, II, 229.



proportion of acceleration is needed to compensate for a slower rate of vulcanisation, and the lack of tack difficulty continues.

Turning to individual synthetic rubbers, GR-S naturally remains by far the most important in view of its general application. The vulcanisation<sup>57</sup> of GR-S has elicited some interesting new chemical details. For example, the addition of water to the batch during milling, a practice adopted to improve the milling itself, has now been shown to have influence on the rate of vulcanisation: below 0.15% of moisture left in the batch vulcanisation is unduly slow, from 0.15% to 0.5% the rate may be erratic, but from 0.5% to 1.0%, which occurs when water is used during milling, uniform results are probable. Various unusual vulcanising agents are forcing themselves into view, including *m*-dinitrobenzene plus litharge, benzoquinone plus lead peroxide, benzenedisulphonyl chloride plus ferric chloride, and ethylxanthogen disulphide. The first two of these are of some practical interest though the tensile qualities of the vulcanisates are low; the third remains so far of academic interest; the last in conjunction with "*N*-cyclohexyl-benzthiazyl-2-sulphur-amide" or with tetramethylthiuram disulphide it is believed may eliminate "many of the serious deficiencies so characteristic of GR-S vulcanisates." Carbon black-GR-S relationships, including broad comparisons of different blacks, form an important part of the *ad hoc* work, but reference may be limited here to the steady development of GR-S-black master batches prepared by adding the black to GR-S at the latex stage.<sup>58</sup> It is now clearly established that such batches give some 30% increase in milling facility, 20% decrease in power consumption, and finished products at least as good as if not better than those obtained by milling carbon into dry GR-S. These latex-mixed batches are coming into bulk use and represent a considerable economy with, incidentally, conspicuous cleaning-up of the factory mill rooms. From a survey of 650 "softeners," as distinct from "peptisers," in GR-S<sup>59</sup> some general conclusions emerge: solvent softeners give more "nervy" mixings as compared with lubricant non-solvents, while for effective dispersion of fillers the softener should have a functional group of high wetting character and a hydrocarbon residue soluble in the rubber, stearic acid being an excellent illustration. Although there is now a considerable body of information on the heat-ageing of GR-S vulcanisates, J. R. Scott<sup>60</sup> concludes that the mechanism of the changes is not yet elucidated. The possibilities suggested include

<sup>57</sup> H. A. Braendle and W. B. Wiegand, *Ind. Eng. Chem.*, 1944, **36**, 724; B., 1944, **II**, 377. D. J. Beaver and M. C. Throdahl, *Rubber Chem. and Tech.*, 1944, **17**, 806. U. K. Ministry of Aircraft Production, Director of Research, *Services Rubber Invest. Mfrs.' Mem.*, M14, 1945.

<sup>58</sup> W. McMahon and A. R. Kemp, *Ind. Eng. Chem.*, 1944, **36**, 735; R. L. Rongone, C. B. Frost, and G. H. Swart, *Rubber Age* [N.Y.], 1944, **55**, 577; B., 1944, **II**, 373; 1945, **II**, 89.

<sup>59</sup> L. E. Ludwig, D. V. Sarbach, B. S. Garvey, jun., and A. E. Juve, *India Rubber World*, 1944, **111**, 55, 180; B., 1945, **II**, 89.

<sup>60</sup> Preprint, *I.R.I. Symposium*, Birmingham, May, 1945. See also J. S. Hunter, *India-Rubber J.*, 1944, **107**, 429, 432; B., 1944, **II**, 377.



after-vulcanisation or increase in combined sulphur, redistribution of combined sulphur to form more cross-linkings, oxygen-bridging, and chain-scission due to oxidation. To what extent and in what combinations these processes operate, and in what ways the ageing conditions and the composition of the rubber affect them, are far from clear, and the available evidence is conflicting. Chemical derivatives of GR-S are becoming known<sup>61</sup>; the chlorinated product compares favourably with chlorinated natural rubber, and the cyclised products obtained by treating GR-S with sulphuric acid, tin chlorides, or boron fluoride in a high-boiling solvent such as phenol, cresol, or naphthalene may find technical applications.

Of the individual synthetic rubbers, GR-I is the latest in bulk use, and its immediate processing remains an urgent difficulty. Vulcanisation, in particular, has been widely investigated.<sup>62</sup> It is necessary to use really powerful accelerators or the *p*-quinonedioxime plus oxidising agent method to get efficient results. Combinations of accelerators such as tetramethylthiuram disulphide 1.0 and zinc diethyldithiocarbamate 1.5 (per GR-I 100 parts) give reasonable rates of vulcanisation at rather high temperatures, *e.g.*, 168°, without premature vulcanisation at 100°. The dioxime method has given factory trouble due to scorching with either lead peroxide or red lead as oxidising agent, and also with the dioxime benzoate instead of the dioxime, but further control of the reaction by the addition of phthalic anhydride has given satisfactory results.

The vulcanisation of GR-M has been in the patent literature<sup>63</sup> in connexion with low-temperature ("self-vulcanising") compositions and cements. The proposals include a mixture of litharge 10 and butaldehydeamine 25 (per GR-M 100), and sulphur chloride 0.1—35 (per GR-M 100). In the latter method, the sulphur chloride may be mixed into a solution or cement of GR-M and brushed on to a supporting surface to dry and vulcanise at room temperature in a period up to 72 hours. The method applies particularly to types of GR-M containing sulphur, formed by polymerising chlorobutadiene in the presence of sulphur.

A claim of considerable practical importance comes from the B. F. Goodrich Co.<sup>64</sup> in connexion with GR-A. This oil-resisting material has obstinately defied being put into any satisfactory solution form, but it is now stated that nitroparaffins, of up to 6 carbon atoms in the alkyl radical, form GR-A solutions substantially free from forming reversible gels on keeping.

<sup>61</sup> H. A. Endres, *Rubber Age* [N.Y.], 1944, 55, 361; B., 1944, II, 377.

<sup>62</sup> F. P. Baldwin, L. B. Turner, and R. L. Zapp, *Ind. Eng. Chem.*, 1944, 36, 791; B., 1945, II, 35. L. H. Cohan, M. Sohn, and M. Steinberg, *Ind. Eng. Chem. [Anal.]*, 1944, 16, 562; C., 1945, 30. Imperial Chemical Industries, Ltd., *Report N-38*, 1944. U.K. Ministry of Aircraft Production, Director of Research, *Services Rubber Invest., Mfrs.' Mem.*, M15, 1945. United States Rubber Co., *Synthetic Rubber Compounding Bull. No. 4*, 1943.

<sup>63</sup> E. I. Du Pont de Nemours & Co., B.P. 566,016, 566,086; B., 1945, II, 91.

<sup>64</sup> U.S.P. 2,360,867.



The organosilicon rubber-like polymers, "silicones," are not exactly new, but during 1945 they have begun to come on the market for experiment and general use, and their remarkable heat-resistant properties<sup>65</sup> have excited widespread interest.

New co-polymers are continually being developed in the present exploratory phase of plastics investigation. In the year under review they include numerous rubber-like products any one of which may turn out to be the rubber of the future; examples are co-polymers of butadiene with butenyl methacrylate,<sup>66</sup> with chlorostyrenes,<sup>67</sup> with cyano-esters,<sup>68</sup> and with aryltriazines<sup>69</sup>; of isobutene with terpin hydrate<sup>70</sup>; of isopropenyltoluene with acrylonitrile<sup>71</sup>; of acrylic esters with small proportions of active monomers such as butadiene, acrylonitrile, or allyl maleate<sup>72</sup>; and of chloroprene with methacrylates.<sup>73</sup> All these products are vulcanisable rubbers.

#### COMPOUNDING INGREDIENTS.

Though review literature is not in general matter for these annual sketches, attention may well be called to a new book with a very full discussion of present knowledge on carbon black.<sup>74</sup> There was a distinct trend a few years ago to submit carbon blacks to various treatments with a view to obtaining improved effects in rubber, but the war apparently cut short such investigations. The subject has been re-opened by the Wingfoot Corporation<sup>75</sup> in a patent for passing black, granular or in pellets, through a non-oxidising atmosphere at 600—800° to remove surface-adsorbed volatile substances, followed by cooling in a non-oxidising atmosphere. Considerable improvement is obtained in abrasion-resistance and flexing qualities; for maximum increase in electrical conductivity the treatment should be at 800—1000°. The process for flocculating black in rubber by holding the mixed stock at 120° or higher has been improved by adding urea, semicarbazide, biuret, or dicyanodiamide to the mixing.<sup>76</sup> With improvement in the technique of preparing specimens for the electron microscope, results of great theoretical importance are emerging,<sup>77</sup> including positive evidence of "structure" in loose

<sup>65</sup> Dow Corning Corp., "Silastic and Silicone Rubber," 1945. R. W. Kolderman, *Canad. Chem.*, 1945, **29**, 147. E. G. Rochow, *Chem. Eng. News*, 1945, **23**, 612. Anon., *Rubber Age* [N.Y.], 1944, **56**, 173; B., 1945, II, 156.

<sup>66</sup> Wingfoot Corp., B.P. 566,497; B., 1945, II, 125.

<sup>67</sup> J. C. Michalek and C. C. Clark, *Chem. Eng. News*, 1944, **22**, 1559; B., 1945, II, 84.

<sup>68</sup> Wingfoot Corp., B.P. 565,813; B., 1945, II, 72.

<sup>69</sup> B. F. Goodrich Co., U.S.P. 2,313,233; B., 1945, II, 36.

<sup>70</sup> Liatex Corp., U.S.P. 2,319,164; B., 1945, II, 118.

<sup>71</sup> Amer. Cyanamid Co., U.S.P. 2,310,961; B., 1944, II, 366.

<sup>72</sup> C. H. Fisher, W. C. Mast, and co-workers, *Ind. Eng. Chem.*, 1944, **36**, 1022, 1027, 1032; B., 1945, II, 85.

<sup>73</sup> E. I. Du Pont de Nemours & Co., B.P. 566,206; B., 1945, II, 86.

<sup>74</sup> I. Drogin, "Developments and Status of Carbon Black," 1945.

<sup>75</sup> B.P. 568,538; B., 1945, I, 251.

<sup>76</sup> United States Rubber Co., U.S.P. 2,315,849-50, 2,315,855-7; B., 1945, II, 157.

<sup>77</sup> W. A. Ladd, *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 642; C., 1945, 79. W. A. Ladd and W. B. Wiegand, *Rubber Age*, 1945, **57**, 299; B., 1945, I, 320. J. N. Mrgudich and R. C. Clock, *Trans. Electrochem. Soc.*, 1944, **86**, 329; A., 1945, I, 113.



carbon as collected from the producers. Thermal carbons have inter-particle bonds referred to as "rod linkage," tending to form at angles of  $120^\circ$ , whereas acetylene and lamp blacks are better described as in persistent clustered chains referred to as "fusion linkage." In contrast, graphite is found in relatively large plate-like crystals, some of them thin enough to be transparent.

A study of fourteen commercial samples of kieselguhr as supplied to the rubber industry as a filler<sup>78</sup> has revealed great variation in chemical properties and in effects in rubber, with some samples very high in grit content and moisture. Tentative specifications are proposed for a satisfactory material.

In the group of antioxidants and preservatives for rubber, numerous additions have been made to the patents in familiar fields, such as amines, aldehyde-amines, ketone-amines, and hydroxy-compounds. Without a complete index to compounds proposed, which now run into thousands, it has become impracticable to pick out any items which suggest fundamental progress as distinct from merely technical novelty in permuting chemical radicals and groups. The following at least reveal the complexity into which investigators have advanced: 1-aryl-3-arylaminoaryl-1:3-dialkylcyclobutanes,<sup>79</sup> di(arylamino)diaryl carbonates,<sup>80</sup> hydroxy-tri- and -tetra-alkylspirobisindanes and anilinomethylindane,<sup>81</sup> di-(1-hydroxy-2-methyl-5-isopropylphenyl) sulphide and mono- or di-sulphides of similar monohydric dialkylphenols,<sup>82</sup> and tetrahydro-polycyclic quinones of condensed ring structure.<sup>83</sup> It should be realised that very few, if any, of these recent antioxidants have received steady trial in factory use.

From the foreign patents that have become accessible in the last year, it is evident that the drive for "peptising" or other chemical "de-vulcanising" agents has been widespread for reclaiming purposes. All the following have been noted: aromatic mercaptans,<sup>84</sup> naphthylthiol and dinaphthyl disulphide,<sup>85</sup> substituted benzenes containing thiophenol groups,<sup>86</sup> and di(hydroxyaryl) sulphides.<sup>87</sup> It has been suggested, also, that the effectiveness of these reagents is increased by allowing scrap rubber to absorb a swelling agent below  $50^\circ$  before adding the reagent and treating the mixture in an autoclave at a raised temperature.<sup>88</sup> Water has been brought into reclaiming processes very prominently,

<sup>78</sup> J. R. Scott, *J. Rubber Res.*, 1945, 14, 11; B., 1945, II, 155.

<sup>79</sup> United States Rubber Co., U.S.P. 2,320,745; B., 1945, II, 168.

<sup>80</sup> *Idem*, U.S.P. 2,380,130.

<sup>81</sup> B. F. Goodrich Co., B.P. 563,479; B., 1944, II, 304. Pennsylvania Coal Products Co., U.S.P. 2,176,881; B., 1945, II, 65.

<sup>82</sup> Monsanto Chem. Co., B.P. 563,175; B., 1944, II, 336.

<sup>83</sup> Wingfoot Corp., U.S.P. 2,379,460.

<sup>84</sup> I. G. Farbenind., F.P. 864,632.

<sup>85</sup> Getefo Ges. f. Techn. Fortschritt m.b.H., F.P. 890,349.

<sup>86</sup> A. Rebmann, Swiss P. 215,952.

<sup>87</sup> United States Rubber Co., U.S.P. 2,372,584.

<sup>88</sup> Soc. Italiana Pirelli, F.P. 865,077.



scrap rubber being heated in water itself<sup>89</sup> under pressure at 240° or in superheated steam<sup>90</sup> at temperatures ranging from 270° to 490°, the latter involving pressures up to 700 lb. per sq. in. This "flash devulcanisation" process is claimed to give improved products.

Crumb rubber has long been a useful cinderella material in the rubber industry and especially during war scarcity; with reclaiming plant inadequate, ground and shredded scrap played an invaluable part. Despite this, detailed information on its properties is almost non-existent in the literature. An extensive examination of the material by J. R. Scott<sup>91</sup> is therefore welcome. Crumb, it appears, has little effect on the plasticity of mixed stocks of natural rubber, GR-S, or GR-A, though it decreases elastic recovery after compression. There is no appreciable interference with vulcanisation, even with thiolbenzthiazole in the crumb. Fineness of crumbing, between 20- and 50-mesh, has no significant effect on the physical properties of the vulcanisates, and the only appreciable change is a shortening and softening of the stress-strain curve, the softening being credited to some adsorption of sulphur and accelerator by the crumb and so compensatable. Some impairment of abrasion- and tear-resistance, as well as the loss in strength, are attributed to the comparative weakness of the bond between crumb and matrix, but an attempt to improve this bond by the use of "wetting agents" during compounding was not successful. Products made by moulding crumb and non-rubber ingredients, without new rubber or reclaim, were measurably better than similar products moulded from reclaim. An explosive new method has been proposed<sup>92</sup> for making crumb from natural or synthetic rubber vulcanisates by dissolving them in ammonia under high pressure and ejecting the solution into a low-pressure chamber, tearing the scrap to fragments.

Numerous softeners of the solvent (swelling) and oil (lubricating) types have been forthcoming in recent years, especially to meet the tough demands of GR-S. They do not involve novel features and an appreciable proportion is still concealed under trade names and symbols. As in reclaiming, specific chemically active substances continue to be suggested, but all recent ones are members of known families, *e.g.*, thiolbenzthiazole and thiolnaphthothiazole,<sup>93</sup> anthranyl-9-mercaptan,<sup>94</sup> and thioanhydrides of alkoxydithionic acids such as butyl- and ethyl-trithiocarbonic acids or allyl-, benzyl-, ethyl-, and methyl-xanthic acids.<sup>95</sup> An investigation has been made of the interesting resin, shellac, in rubber.<sup>96</sup>

<sup>89</sup> H. Solakian, U.S.P. 2,317,491; B., 1945, II, 126.

<sup>90</sup> J. and S. C. Lewis, B.P. 569,659; B., 1945, II, 286. P. D. Bowers, *Rubber Age* [N.Y.], 1944, 55, 392. J. Hirschberger, U.S.P. 2,313,146; B., 1944, II, 380.

<sup>91</sup> *Trans. Inst. Rubber Ind.*, 1944, 20, 53; B., 1944, II, 373.

<sup>92</sup> Gen. Motors Corp., U.S.P. 2,318,693; B., 1945, II, 126.

<sup>93</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,190,587; B., 1945, II, 196.

<sup>94</sup> I. G. Farbenind., Belg.P. 452,919.

<sup>95</sup> Monsanto Chem. Co., B.P. 568,723; B., 1945, II, 286.

<sup>96</sup> J. R. Scott, *J. Sci. Ind. Res., India*, 1945, 3, 345; B., 1945, II, 194.



This material does not facilitate "breakdown" or processing, and causes marked calender grain which, however, disappears during vulcanisation. The acidic character of shellac reduces the rate of vulcanisation, a disadvantage overcome by means of an alkaline filler such as magnesium oxide. The principal effect on the physical properties of the product is a large increase in hardness.

#### VULCANISED RUBBER.

Reference was made in last year's Annual Report to mathematical formulæ developed to give quantitative interpretations of the filler reinforcement of rubber. H. M. Smallwood<sup>97</sup> has added a new equation indicating that for spherical particles at low-volume loadings, with some simple limitations to avoid extreme cases, the effect of the filler on the modulus is independent of particle size, while increase in modulus is directly proportional to volume loading. Soft blacks and whiting agree quantitatively with these conclusions. Channel blacks do not satisfy the equation, a fact attributed to their flocculation in the rubber. Clay presents anomalies due to its acicular particles. Zinc oxide fails to agree, perhaps because of its abnormal effect on the vulcanisation reaction and consequently on the modulus. E. Guth,<sup>98</sup> on the assumption that a filler dispersion consists of (i) spheres, or (ii) ellipsoids including plates and rods, suspended in a continuous rubber matrix, has obtained expressions for the viscosity, Young's modulus, stress-strain curve, and dielectric constant of the suspension as linear functions of low-volume loadings, and as quadratic functions of high loadings. The formulæ involve a decrease in tensile strength for very low loadings due to stress concentrations around the particles; the subsequent increase at higher loadings is attributed in the case of carbon black to the formation of particle chains. The formulæ involve, also, similar stress-strain curves at various loadings. All these features have been verified experimentally. This theory of reinforcement becomes similar to Einstein's theory of the viscosity of colloidal solutions and Maxwell and Rayleigh's theory of dielectric properties.

In connexion with the ageing of vulcanised rubber, attention has been directed mainly in the last year to ozone-cracking.<sup>99</sup> J. M. Ball and co-workers have shown that this kind of cracking varies little between 25° and 37.5°, though no cracking occurs at -18°. E. F. Powell and E. Gough have advanced a theory that the severity and distribution of the cracks depend on two main factors—the distribution of the surface-film strength as modified by exposure, and the rate of propagation of initially small cracks which is dependent on the tearing-resistance of

<sup>97</sup> *J. Appl. Physics*, 1944, 15, 758; B., 1945, II, 323.

<sup>98</sup> *Ibid.*, 1945, 16, 20; B., 1945, II, 228.

<sup>99</sup> J. M. Ball, R. A. Youmans, and A. F. Rausell, *Rubber Age* [N.Y.], 1944, 55, 481; B., 1944, II, 374. E. F. Powell and V. E. Gough, *Preprint, I.R.I. Symposium, Birmingham*, 1945. R. G. Newton, *J. Rubber Res.*, 1945, 14, 27, 41; B., 1945, II, 229.



the rubber. This theory is said to have a parallel in metal corrosion. R. G. Newton stresses the difference between "cracking" due to ozone scission of bonds, where the cracks form at right-angles to the applied stress, and "sun-cracking" (preferably "crazing"), where the fissures run in any direction in an oxidised surface layer. For the former light is not only unnecessary but has a retarding effect. Crack growth is shown to occur by coalescence of small cracks followed by collapse of other small cracks in the vicinity of the large ones formed. The greater growth tendency of cracks at a "critical elongation" is explained on the argument that the smaller number of cracks at the lower "critical elongation" is unable to relieve the surface strain without gaping more widely than do the more numerous cracks at higher elongations. Gaping then facilitates the entry of ozone to deepen the cracks and increases the difference between the two cases. The two papers just reviewed are directly opposed as to means of minimising crack formation; Powell and Gough consider the best means is by compounding for high tear-resistance, while Newton believes compounding is of little use and stands for surface coating protection against ozone attack.

Contributions to the problem of bonding rubber to metals have been numerous in the year under review, but it is difficult to see any fundamental advance. Most of the work relates to improved detail study of known processes, particularly the use of brass plating and of adhesive or bonding layers. All the familiar bonds have cropped up, some more than once: depolymerising agents including copper in the rubber layer at the metal-rubber face, cyclised rubber, chlorinated rubber, rubber hydrochloride, and a respectable range of vinyl and other polymers or condensation products. Specific new adhesives<sup>100</sup> to add to the above include aldehyde resins as primers for latex coatings, alkyd resins mixed with iron oxide followed by a layer of rubber latex containing hæmoglobin, and chlorinated rubber containing 1 : 3-dichloro-5 : 5-dimethylhydantoin.

#### *Analysis and Testing.*

The systematic scheme for identifying synthetic rubbers, as discussed in last year's Annual Report, has not been further elaborated, but it may be noted that two of its basic tests,<sup>101</sup> the "reaction time" in a mixture of nitric and sulphuric acids, and the ratios of swelling in benzene, light petroleum, and aniline, have been reported in detail in respect of the ground work undertaken when formulating the general scheme. The system has been reinforced, also, by further confirmatory tests; *e.g.*, Weber's colour test for natural rubber, namely, the development of a pronounced violet colour on adding a few drops of bromine followed by a small quantity of phenol, and warming, has been found<sup>102</sup> specific to an active methylene group next to a double bond, so that positive results

<sup>100</sup> E. I. Du Pont de Nemours & Co., U.S.P. 2,321,889; Amer. Lurgi Corp., U.S.P. 2,320,937; B., 1945, II, 197, 151. United States Rubber Co., U.S.P. 2,373,308.

<sup>101</sup> L. F. C. Parker, *J.S.C.I.*, 1944, **63**, 378; 1945, **64**, 65; C., 1945, 110, 174.

<sup>102</sup> L. F. C. Parker and W. C. Wake, *Analyst*, 1945, **70**, 175; C., 1945, 174.



are obtained with guttapercha, balata, and GR-M, while rubber hydrochloride and GR-I give a faint reaction. A rapid confirmation of GR-M has been proposed<sup>103</sup> by dry-distilling the sample from a crucible nearly covered with a potassium chromate paper; chlorine in the distillate bleaches the paper. The various types of GR-P fall into two main classes, disulphides and tetrasulphides. L. F. C. Parker<sup>104</sup> has shown that the disulphides contain about 50% of sulphur substantially resistant to sodium sulphite, whereas the tetrasulphides contain about 80% of sulphur, half of which is easily removable by the sulphite. The two classes are thus easily differentiated by boiling the acetone-extracted rubber for 12 hours with sodium sulphite solution, the resultant thio-sulphate being titrated with iodine.

The urge to modify existing methods of quantitative analysis has been directed in 1945 largely to the apparatus used for acetone extraction.<sup>105</sup> The widely used apparatus of Schidrowitz and Kaye<sup>106</sup> employs a rather complicated condenser fused to a wide glass tube which rests in a mercury seal on the neck of the flask holding the acetone. T. H. Messenger has simplified the arrangement by using a separate wide tube with an externally cooled condenser resting on a bulbous enlargement in the upper end; either member is readily replaceable where breakages are apt to occur as in a battery of extractors. W. E. Boyd has provided a neat thimble support and a solvent recovery take-off in the U.S. Underwriters' extraction apparatus. L. F. C. Parker<sup>104</sup> has observed that vulcanisates containing polyisobutene are amenable to extraction since the polybutene, not being vulcanised, can be separated quantitatively in 24 hours with light petroleum, b.p. 40—60°.

A quick method for determining total and combined sulphur in GR-I<sup>107</sup> follows well-trodden paths. One sample is burned in oxygen and the resultant sulphur dioxide is oxidised to sulphuric acid with sodium hypobromite and precipitated as barium sulphate; a second sample is extracted in a Soxhlet apparatus with methyl ethyl ketone and the extracted rubber is burnt as before, the extractable sulphur being obtained by difference.

The greatly increased use of the accelerator, cyclohexylbenzthiazylsulphinimide, which is an oxidised cyclohexylamine derivative of thiolbenzthiazole, has created the need for a method of determination in master batches without interference from the equally widely used thiolbenzthiazole. J. Kay and P. J. C. Haywood<sup>108</sup> have elaborated a specific reaction, the reduction of the extracted sulphinimide with isopropyl

<sup>103</sup> D. Roberts, *Rubber Age and Synthetics*, 1945, **26**, 22; C., 1945, 110.

<sup>104</sup> *India Rubber J.*, 1945, **108**, 387; C., 1945, 110.

<sup>105</sup> T. H. Messenger, *J. Rubber Res.*, 1944, **13**, 97; W. E. Boyd, *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 721, 722; C., 1944, 172; 1945, 150.

<sup>106</sup> *J.S.C.I.*, 1907, **26**, 127.

<sup>107</sup> J. Rehner, jun., and J. Holowchak, *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 98; C., 1944, 172.

<sup>108</sup> *India Rubber J.*, 1945, **109**, 185, 188; C., 1945, 245.



alcohol and sodium and titration of the resultant *cyclohexylamine* with hydrochloric acid. The method requires an empirical correction factor to allow for a small loss of accelerator proportional to the amount under test.

The conditions of the "standard" accelerated ageing test have not been disturbed recently, but J. M. Buist and G. N. Welding<sup>109</sup> have contributed notes on the use and abuse of the test. It is suggested that there are really three different types of ageing change—shallow or surface changes of negligible importance in regard to the mechanical properties of thick articles, deep surface changes, and changes occurring uniformly throughout the rubber. The accelerated ageing test selected for use should be appropriate to the kind of change involved in service, the most common confusion being between the effects of light and of exposure to the atmosphere. Insufficient attention is paid, also, to the loss of homogeneity in test samples as ageing progresses. The decomposition of uranyl oxalate by radiant energy, used in the A.S.T.M. actinometer for measuring sunlight and other light in ageing and weathering tests on rubber, has been studied in relation to the spectral sensitivity of the reaction.<sup>110</sup> It is concluded that the instrument is unsatisfactory for comparing different sources of energy, but is reliable for controlling the constancy of any one source.

An unusual test method<sup>111</sup> has been added to the rubber laboratory in a simple process of blowing powders against a Bunsen flame to obtain evidence as to the possibility of dust explosions among many of the materials commonly used by the industry.

<sup>109</sup> *Preprint, I.R.I. Symposium, Birmingham, 1945.*

<sup>110</sup> F. T. Bowditch, C. E. Greider, and C. G. Ollinger, *Proc. Amer. Soc. Test. Mat.*, 1942, **42**, 845; C., 1944, 172.

<sup>111</sup> D. F. Twiss and W. McCowan, *India-Rubber J.*, 1944, **107**, 292; B., 1944, **II**, 334; C., 1944, 208.



## LEATHER.

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By far the greatest number of papers published during the year have been directly prompted by war needs. Great interest has been taken in the search for and investigation of new supplies of natural vegetable tanning materials and in substitute tanning materials such as syntans, showing where one of the major difficulties due to war shortage lay. Of the very serious shortage of hides and skins nothing can be said, as there was nothing in the leather industry to be done. However, strenuous efforts were put forth to make the most of the material that was available, maintaining quality in spite of shortages and utilising waste leather. In addition, there was much more fundamental work done than might have been expected under the circumstances.

Some of the work published in Germany during the war has now become available, and this indicates that there, too, energetic attention had been paid to investigations of substitute tanning materials.

### HIDES, SKINS, AND PRESERVATION.

Although hides and skins have been known to consist of interweaving bundles of fibres it has not been generally realised that there is a fundamental pattern of interweaving, different in different animals. The layout of fibres in skins has been considerably elucidated in the case of calf, sheep, and goat skin<sup>1</sup> by using a striking and interesting method of tracing out the lines of cleavage and tension in the skin,<sup>2</sup> and shown to be closely related to the directions of hair growth on the animals. The tension lines have been shown to be related to the directions of the muscle fibres beneath the skin in the case of calf.<sup>3</sup>

Curing salts from various sources and their effects on the leather made from skins preserved by them are matters which still need further study. From India, S. S. Aiyar<sup>4</sup> has reported the increasing use of bittersalts in preserving hides and skins. The relative proportions of different sodium compounds in such salts vary considerably according to the source, the composition of the salt from Sambhar salt lake being given as NaCl 62.1, Na<sub>2</sub>SO<sub>4</sub> 21.8, Na<sub>2</sub>CO<sub>3</sub> 12, and NaHCO<sub>3</sub> (+ small amounts of Na<sub>2</sub>S and Na<sub>2</sub>SiO<sub>3</sub>) 4.1%. Sodium sulphate itself is considered to have a quite good preservative action on hides<sup>5</sup> and small amounts of

<sup>1</sup> G. O. Conabere, *J. Soc. Leather Trades' Chem.*, 1944, 28, 270; B., 1945, II, 92.

<sup>2</sup> Cox, *Brit. J. Surg.*, 1941, 29, 234.

<sup>3</sup> G. O. Conabere, *J. Soc. Leather Trades' Chem.*, 1944, 28, 3.

<sup>4</sup> *J. Sci. Ind. Res. India*, 1944, 3, 198; B., 1945, II, 125.



the carbonate (up to 2% anhydrous) have been added to curing salts with a beneficial effect. At the same time the effects of higher amounts of alkali on cured goods especially after a period of storage have not been fully investigated, and it is recommended that until further evidence of the effects of such salts on the skins is obtained, salt containing more than 3% of sodium carbonate should not be used.\*

Some years ago D. Jordan Lloyd and M. E. Robertson<sup>6</sup> described a method of disinfecting dry hides from anthrax by means of drumming in a warm lime liquor containing 1% of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , which had proved successful in works-scale trials as regards both the sterilisation of the hides and their condition after disinfection. Work on the problem of anthrax disinfection has been continued by W. Hausam, R. Schnegg, and T. Schlindler<sup>7</sup> making use of thiocyanate solutions of different concentrations and also Rohzephirol. The most effective thiocyanate solution was found to be a mixture of M./16 sodium thiocyanate and N./8 hydrochloric acid containing 2.5% of sodium chloride, but 0.5—0.75% of Rohzephirol was even more effective and less damaging to the skins.

W. Grassmann and W. Hausam<sup>8</sup> have previously emphasised the necessity of comparative purity in the preserving salts used on hides and skins, and have again done so in a report on the effects of various proprietary substances in the curing of pig and calf skins compared with salt and salt plus naphthalene and soda which had been previously advocated for pig skins.<sup>9</sup> W. Hausam<sup>10</sup> has also described a method of investigating curing salts in the laboratory. Catadyn silver preparations have been found to give disappointing results both in the laboratory and in large-scale tests<sup>8</sup> with calf skins. It is believed that curing salt should be free from calcium and magnesium salts, carbonates, sand, alumina, and iron as they have a deleterious effect on the preservative power of the salt. J. Babička and E. Treusch<sup>11</sup> have shown, for instance, that the bactericidal action of sodium ions can be prevented by calcium, magnesium, and potassium ions; in the case of *Staphylococcus pyogenes* the toxic effect of sodium ions can be completely removed by the presence of calcium ions.

Hide beetles can be a source of considerable loss. In Canada<sup>12</sup> *o*- and *p*-dichlorobenzene have been found to be successful in controlling the particularly serious pest *Dermestes vulpinus* F.

\* At the B.L.M.R.A. Laboratories high alkalinity in curing salts has been found to have disastrous effects.

<sup>5</sup> D. Jordan Lloyd, *Bull. Imp. Inst.*, 1937, 22.

<sup>6</sup> D. Jordan Lloyd and M. E. Robertson, *J. Soc. Leather Trades' Chem.*, 1930, 14, 641; *ibid.*, 1931, 15, 586.

<sup>7</sup> *Zentr. Bakt.*, 1944, I, 151, 193; B., 1944, II, 381.

<sup>8</sup> *Collegium*, 1942, 358; B., 1946, II, 145.

<sup>9</sup> W. Hausam, *ibid.*, 1941, 153; B., 1946, II, 106.

<sup>10</sup> *Ibid.*, 1942, 377; C., 1946, 24.

<sup>11</sup> *Ibid.*, 1941, 241; B., 1946, II, 106.

<sup>12</sup> F. H. Walker, *J. Kansas Entomol. Soc.*, 1944, 17, 7; *J.A.L.C.A.*, 1945, 40, 291.



## COLLAGEN AND GELATIN.

Additional justification for the amphoteric ionic concept of protein behaviour has been put forward by K. H. Gustavson<sup>13</sup> as a result of his recent studies comparing the different degrees of affinity of the hide protein for mineral acids, which are reversibly held by it, and for ligno-sulphonic acids and condensed phenolsulphonic acids, which are mainly irreversibly fixed by it.

Whereas the reaction of mineral acid is solely a function of the hydrogen-ion concentration of the system, the fixation of sulphonic acids is not solely controlled by the pH value of the system. The stability of the bond formed between basic protein groups and the anion of the sulphonic acid is of equal or greater importance, and is the dominating factor between pH 4 and 7. The different degree of affinities of the anions of strong acids reversibly combined with the protein is the likely cause of the different shapes of the acid-binding curves. The sulphonic acids show a much higher binding equivalent than hydrochloric acid, particularly between pH 2.5 and 5, and in addition a marked fixation of salts of sulphonic acids and inactivation of the basic protein groups by them is found between pH 5 and 7, the isoelectric zone. This reaction is shown to be due to the affinity of the anion of the acid for the basic protein groups. The protein fixes a sulphonate of very much lower ratio of metal cation to anion of sulphonic acid than that of the original compound as a consequence of the hydrolysis of the cation-carboxyl group linkage. The fixation of neutral sulphonates cannot be explained by the classical theory of protein reactivity.

In studies measuring the water content of untanned and tanned hide powder, H. C. Holland<sup>14</sup> has found that the equilibrium water content of the untanned hide powder is unaffected by pre-treatment in a series of buffers having pH 1—12, but both tanned and untanned hide powder have a reduced value after dehydrating by heating at 105°. When untanned hide powder is rehydrated after complete dehydration only the peptide groups take up water again. It is concluded that protein side-chains can remain hydrated when combined with tannins.

The reactions of a number of standard and deamidised proteins with formaldehyde under acid conditions have been studied by R. L. Wormell and M. A. G. Kaye,<sup>15</sup> who have concluded that under acid saline conditions the formaldehyde combines with the amide groups present.

H. Mosimann and R. Signer<sup>16</sup> have calculated the molecular weights of two gelatin fractions from determinations of the sedimentation equilibrium in the ultracentrifuge. Evidence suggests that one type (M.F.I.) which shows very distinct polydispersity consists of net-like cross-linked

<sup>13</sup> *Svensk Kem. Tidskr.*, 1945, 57, 36; *J.S.L.T.C.*, 1945, 29, 238.

<sup>14</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 70; *B.*, 1945, II, 231.

<sup>15</sup> *J.S.C.I.*, 1945, 64, 75; *A.*, 1945, II, 264.

<sup>16</sup> *The Svedberg Mem. Vol.*, 1944, 465; *A.*, 1945, III, 316.



molecules and that the other (V,1) which is obtained in nearly uniform dispersity consists of simple linear or bunched molecules.

Based on the tendency of the polar groups to bind dyes of the opposite charge, micro-analytical methods have been developed for the determination of the number of acid and basic groups of both soluble and insoluble proteins.<sup>17</sup> J. L. Stokes, M. Gunness, I. M. Dwyer, and M. C. Caswell<sup>18</sup> have published a micro-biological method and A. E. Sobel, A. Hirschman, and L. Besman<sup>19</sup> a micro-titration method of determining amino-acids, and H. S. Olcott<sup>20</sup> a method for determining glutamic acid. N. V. Chernov<sup>21</sup> has, with reason, called into question the factor used in the Kjeldahl estimation of hide substance. R. Consden, A. H. Gordon, and A. J. P. Martin<sup>22</sup> have described an interesting qualitative analysis of proteins (hydrolysate) by a partition chromatographic method using paper.

A. Rousselot<sup>23</sup> has described the elimination of aluminium, magnesium, calcium, barium, and sulphate from gelatin by the successive use of exchangers. For hydrogen a formaldehyde-resorcinol resin was used, and for hydroxyl, products of condensation of aldehydes and aromatic bases.

#### PROCESSES PRECEDING TANNAGE.

*Soaking and Liming.*—Little has appeared on this subject, although a number of papers on practical aspects of these processes have appeared in *Collegium* during the war years.

W. Hausam and W. Schindler<sup>24</sup> have described the soaking of goat skin in water with the addition of wetting-out agents and disinfectants, some of which interfered with the action of the wetting agents.

Considerable interest has been taken in conservation of hair during unhairing and V. Kubelka, L. Masner, and M. Tomišek<sup>25</sup> have investigated the extent of hair damage in different unhairing processes. They have used a chemical method of determining hair damage, depending on the combination of certain free reactive groups of damaged hair with a diazo-compound of *p*-nitroaniline, and confirm the fact of the damaging effect of sodium sulphide on the hair. J. A. Sagoscheno<sup>26</sup> has put forward a method of drum liming by which the hair is saved, but this also involves reducing the amounts of sodium sulphide used. W. Grassmann and O. Engel<sup>27</sup> discussed treatment of hair to make it "felt" and "full."

<sup>17</sup> H. Fraenkel-Conrat and M. Cooper, *J. Biol. Chem.*, 1944, **154**, 239; C., 1944, 193.

<sup>18</sup> *Ibid.*, 1945, **160**, 35; C., 1946, 49.

<sup>19</sup> *Ibid.*, **161**, 99; C., 1946, 121.

<sup>20</sup> *Ibid.*, 1944, **153**, 71; C., 1944, 193.

<sup>21</sup> *Legkaya Prom.*, 1942, **2**, 23; *Chem. Abs.*, 1944, 5429.

<sup>22</sup> *Biochem. J.*, 1944, **38**, 224; C., 1944, 193.

<sup>23</sup> *Compt. rend.*, 1943, **216**, 54; B., 1945, **II**, 66.

<sup>24</sup> *Collegium*, 1942, 201; B., 1946, **II**, 144.

<sup>25</sup> *Ibid.*, 1943, 67; B., 1946, **II**, 144.

<sup>26</sup> *Ibid.*, 169; B., 1946, **II**, 145.

<sup>27</sup> *Ibid.*, 113; B., 1946, **II**, 144.



They find that calf or ox hair obtained by sweating or fellmongering methods cannot be "fulled" if undamaged by lime or sulphide. A good fullability appears to depend on a fairly complete rupture of the disulphide linkage in cystine. W. Grassmann and co-workers<sup>28</sup> have previously reported results of large-scale tests of various fellmongering processes compared with different methods of shearing in their effects on the wools and leathers obtained. Painting, a biological process, and a combined sweating-painting process all gave better leather and wool than shearing.

E. H. Riddle<sup>29</sup> has reviewed the chemistry and uses of methylamine and D. W. Jayne, jun.,<sup>30</sup> has patented an unhairing process which involves the presence of a substituted guanidine sulphide formed *in situ* in the lime liquor.

J. Pfannmuller and H. Schleich<sup>31</sup> have patented a mixture of a relatively insoluble alkaline-earth sulphide, *e.g.*, calcium sulphide (5—10%), a neutralising agent, *e.g.*, ammonium sulphate (60—80%), and a proteolytic enzymic preparation absorbed on wood flour for unhairing.

*Deliming and Bating.*—Following up previous work,<sup>32</sup> in which most of the theories then held about the function or functions of bating were critically examined and found wanting, H. Anderson<sup>33</sup> has, in a neat experiment on goat skin, shown that the bating efficiency of four specially selected enzymes was directly related to their power to digest involuntary muscle fibres. It seems inescapable to conclude that this accounts for the well-known selective action of bates on the grain layer of skins. Regarding the softening action of bates on whole skins, the "mechanism" of the effect is not quite so clear, but there is some evidence indicating that the "fallen" feel of a bated skin is connected with a mild peptisation of the collagen fibres.

#### VEGETABLE TANNING MATERIALS.

World-wide efforts to increase the amounts of natural vegetable tanning materials available continue to be reported. New sources of tannin have been investigated in the U.S.A., India, South Africa, France,<sup>34</sup> Spain, Germany,<sup>35</sup> and Russia.<sup>36</sup>

Tannin has been extracted from wild and cultivated canaigre roots<sup>37</sup> and has given satisfactory results in preliminary experiments in tanning light leather. Tannin has also been obtained from Western hemlock

<sup>28</sup> W. Grassmann, H. Schelz, and O. Engel, *Collegium*, 1941, 337; B., 1946, II, 106.

<sup>29</sup> *Chem. Industries*, 1944, 55, 209; B., 1944, II, 341.

<sup>30</sup> U.S.P. 2,192,380; B., 1945, II, 255.

<sup>31</sup> U.S.P. 2,326,360; B., 1945, II, 326.

<sup>32</sup> H. Anderson, *J. Soc. Leather Trades' Chem.*, 1941, 25, 35.

<sup>33</sup> *Ibid.*, 1945, 29, 209; B., 1946, I, 26.

<sup>34</sup> P. Chambard, *Doc. Sci. Tech. Ind. Cuir*, 1942, 7; B., 1946, II, 65.

<sup>35</sup> H. Czetsch, Lindenwald, and F. Kuntze, *Collegium*, 1943, 140.

<sup>36</sup> N. V. Boltenkov, *Legkaya Prom.*, 1941, 1, 48.

<sup>37</sup> J. S. Rogers and G. A. Russell, *J. Amer. Leather Chem. Assoc.*, 1944, 39, 467; J. S. Rogers and E. C. Stevenson, *ibid.*, 479; B., 1945, II, 159.



bark<sup>38</sup> (*Tsuga heterophylla*), the solubility of the extract being increased by the use of sodium bisulphite. A. Russell<sup>39</sup> has published a summary of the commercial uses of several natural tanning materials in the south-eastern U.S.A. The materials described include buttonwood (*Conocarpus erecta*, L.), California redwood (*Sequoia sempervirens*), Western (see above) and Eastern hemlock (*Tsuga canadensis*), and Australian pine (*Casuarina equisetifolia*).

F. L. Hahn<sup>40</sup> has investigated the tannin content of the powder (57.5%), kernels, and husks (31%) of the pods of algarobilla (probably *Balsamocarpum brevifolium*) and also points out that the kernels yield an edible oil of high quality. Other materials investigated include the Hottentot fig,<sup>41</sup> spruce,<sup>42</sup> Turkmen rhubarb,<sup>36</sup> and *Eucalyptus* sp. (*E. occidentalis*, var. *astringens* and var. *citriodora*).<sup>34</sup>

In India, B. M. Das<sup>43</sup> has reviewed the possibilities of producing more of the native tanning materials which give superior tans but which have been largely displaced in the last 30 years by imported wattle (*Acacia mollissima* and *A. decurrens*, var. *mollis*). Several materials which could be cultivated, peeled, and made into extracts by modern methods are suggested, e.g., Avaram (*Cassia auriculata*), Konam (*Cassia fistula*), babul (*Acacia arabica*), myrobalans (*Terminalia chebula*), and mangrove (*Ceriops roxburghiana*, *C. candolleana*, *Rhizophora mucronata*, and *Bruguiera gymnorrhiza*). Wattle will also grow freely in Southern India and could be cultivated.

In endeavouring to obtain the maximum possible quantity of soluble tannin when making extracts, darkening of the tannins tends to occur and effective methods of treating extracts to improve (i.e., lighten) their colour are important. Myrobalan extract<sup>44</sup> (Bhimlitan) decolorised by treatment with aluminium sulphate at 65.6° for 30 minutes has been found to produce a leather of improved colour, without appreciable loss of tannin, whereas if the extract were similarly treated with lead acetate a good coloured leather was produced, but there was a considerable loss in tannin. T. D. Braunschweig<sup>45</sup> has studied the treatment of quebracho extract by sulphite and bisulphite to improve solubility and colour, and has put forward a mechanism to explain the effects observed.

A. Cheshire<sup>46</sup> has intensively studied mimosa liquors which oxidise and darken in colour when exposed to air in the dark but not when

<sup>38</sup> E. F. Potter, K. T. Williams, T. L. Swenson, and I. C. Feustel, *Ind. Eng. Chem.*, 1944, 36, 1146; B., 1945, II, 91. W. Pittam, *Pacific Pulp and Paper Ind.*, 1944, 18, Dec., 35; B., 1945, II, 197.

<sup>39</sup> *J. Amer. Leather Chem. Assoc.*, 1945, 40, 110; B., 1945, II, 197.

<sup>40</sup> *Ciencia*, 1943, 4, 242; B., 1944, II, 242.

<sup>41</sup> T. Y. Hum and R. Pratt, *Plant Physiol.*, 1944, 19, 384; B., 1945, II, 66.

<sup>42</sup> W. Kantara and W. Grassmann, *Collegium*, 1943, 79; W. Hausam and W. Kantara, *ibid.*, 130; B., 1946, II, 143.

<sup>43</sup> *J. Sci. Ind. Res. India*, 1944, 2, 196; B., 1944, II, 336.

<sup>44</sup> E. Knew and A. T. Ray, *J. Soc. Leather Trades' Chem.*, 1944, 28, 136; B., 1944, II, 38.

<sup>45</sup> *J. Amer. Leather Chem. Assoc.*, 1945, 40, 185; B., 1945, II, 287.

<sup>46</sup> *J. Soc. Leather Trades' Chem.*, 1944, 28, 251; B., 1945, II, 66.



dissolved and heated *in vacuo*. The rate of darkening is accelerated by heat and exposure to light and retarded by reducing the pH to 3.0. Oxidation is accompanied by the formation of acid non-tannin material. It is interesting that mimosa darkens rapidly when heated with sulphur trioxide, and also that oxalic acid has no specific action in retarding oxidation apart from its pH effect. Fixed mimosa tannin stripped from leather is largely but not completely oxidised.

Green mimosa bark<sup>47</sup> and several other tannins have been investigated by the same author.<sup>48</sup> Specially purified tannins have been found to develop acid when heated in the presence of acid, alkali, or hydrogen peroxide. Also, skivers tanned with various pure pyrogallol and pyrocatechol tannins all developed acid on exposure at 100° for 3 weeks in the dark.<sup>44</sup>

Tannin and phlobaphen have been isolated from redwood (*Sequoia sempervirens*) and their chemical natures investigated.<sup>49</sup> The tannin was found to be a phlobatannin and the phlobaphen a condensation product of it in which both phenolic and aliphatic hydroxyl groups are involved. Polarographic studies of solutions of quebracho extract and of pyrocatechol have been described by A. K. Vlček, V. Mansfield, and D. Krkošková.<sup>50</sup>

While British chemists were earnestly seeking to make quebracho extract into a satisfactory substitute for chestnut extract, in France chemists were treating chestnut to make it a satisfactory substitute for quebracho.<sup>51</sup>

#### SYNTANS.

In addition to the search for natural vegetable tanning materials, considerable activity has been developed in the search for synthetic tanning materials and several patents<sup>52</sup> have been taken out for synthetic materials to be used either for the whole or for part of the tanning process. Addition of a naphthalenesulphonic acid syntan to the dyebath for increasing penetration and reducing surface colour has also been recommended.<sup>53</sup> H. G. Turley<sup>54</sup> has experimented with a phenolsulphonic acid type of syntan containing 31.0% of tans and having pH 3.2. He found that leather tanned with it gave a rather higher degree of tannage than leather tanned with either chestnut or quebracho under identical conditions, and it also had a good plumpness and good fibre strength.

<sup>47</sup> A. Cheshire, *J. Soc. Leather Trades' Chem.*, 1944, **28**, 281; B., 1945, II, 91.

<sup>48</sup> *Ibid.*, 1945, **29**, 14; B., 1945, II, 159.

<sup>49</sup> M. A. Buchanan, H. F. Lewis, and E. F. Kurth, *Ind. Eng. Chem.*, 1944, **36**, 907; B., 1945, II, 65.

<sup>50</sup> *Collegium*, 1943, 231, 245; B., 1946, II, 143.

<sup>51</sup> *Bull. Assoc. Franc. Chim. Ind. Cuir*, 1941, 241.

<sup>52</sup> B.P. 563,288; B., 1945, II, 66. U.S.P. 2,320,678; B., 1945, II, 198. U.S.P. 2,191,943; B., 1945, II, 255. B.P. 569,909; B., 1945, II, 327. B.P. 565,627; B., 1945, II, 127. U.S.P. 2,316,714; B., 1945, II, 67. U.S.P. 2,322,959; B., 1945, II, 231.

<sup>53</sup> T. E. Nestler and G. L. Royer, *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 40; B., 1945, II, 197.

<sup>54</sup> *Ibid.*, 58; B., 1945, II, 197.



H. Herfeld<sup>55</sup> has described 19 new synthetic tanning materials—substitutes for vegetable tanning materials—and has put forward a number of conditions with which such materials should comply.

### TANNING.

A number of papers contributing to the elucidation of the mechanisms involved in tanning have appeared, many of them stressing the necessity for the incorporation into the hide protein of groups essentially non-ionic in character to enable true tannage (measured by an increase in the shrinkage temperature) to be brought about.

K. H. Gustavson<sup>56</sup> (see also Collagen section<sup>13</sup>) has described experiments with lignosulphonic acids and lignin extracts which are irreversibly fixed (electrovalently) by the hide but which the author considers do not "tan" because they do not produce the required degree of improvement in hydrothermostability (increase in shrinkage temperature). At the same time H. C. Holland<sup>14</sup> has come to the conclusion that protein side-chains can remain hydrated when combined with vegetable tannins.

The subject is, however, still extremely complex and many possibilities of "incorporation" of tanning materials into hides and skins undoubtedly exist,<sup>57</sup> the two extremes being the electrovalent chemical combination of the tanning material with the hide protein, as in the case of the lignosulphonic acids,<sup>56</sup> and mere mechanical deposition inside the hide spaces, as L. Seligsberger<sup>58</sup> has concluded is the case when sulphur is precipitated into skins by treatment with sodium thiosulphate and hydrochloric acid.

*Vegetable Tanning.*—E. R. Theis<sup>59</sup> has studied factors influencing vegetable tanning and points out that leather tanned in quebracho solution shows two points of minimum swelling, viz., at pH 5.0 and 7.5 approximately, corresponding with the two minimum points for fixation of vegetable tannin. It is supposed that at pH 4.0—7.0 the  $\text{NH}_3^+$  groups in adjacent peptide chains are linked together by combination with anionic groups in the vegetable tannin, whereas, at lower pH values, each vegetable tannin molecule is fixed by only one  $\text{NH}_3^+$  group. The maximum shrinkage temperature occurs in the zone of minimum swelling and fixation of tannin. The same author has also studied the collagen-benzoquinone reaction and its relation to vegetable tanning.<sup>60</sup> Fixation increases with time and concentration of benzoquinone. The reaction is of two types, one rapid, which attains maximum fixation at pH 7.0, the other a slow oxidation giving maximum fixation at pH 5.1. The author considers this to be due to different rates of polymerisation and oxidation of the benzoquinone in contact with the pelt under the different

<sup>55</sup> *Collegium*, 1943, 145; B., 1946, II, 106.

<sup>56</sup> *Tekn. Tidskr. Uppl. C, Kemi*, 1943, 73, 59; *Chem. Abs.*, 1944, 5427.

<sup>57</sup> D. Jordan Lloyd, *J. Soc. Leather Trades' Chem.*, 1943, 27, 20.

<sup>58</sup> *J. Amer. Leather Chem. Assoc.*, 1945, 40, 121; B., 1945, II, 198.

<sup>59</sup> *Ibid.*, 1944, 39, 319; B., 1944, II, 381.

<sup>60</sup> *Ibid.*, 1945, 40, 136; B., 1945, II, 230.



conditions, a view that is supported by spectrophotometric absorption curves. The isoelectric points of the tanned and untreated collagen are similar and the fixation of vegetable tannin between pH 5.0 and 8.0 is analogous to the fixation of benzoquinone by collagen.

P. O. Chang, C. T. Yen, and H. L. Chen<sup>61</sup> have contributed the observation, by investigating the sorption of total soluble matter of Chinese valonia by original and deaminated hide powders at pH 2.42 and 2.70, that, at the latter pH, the deaminated hide powder takes up considerably less than the original. The swelling of the hide powders appears to govern the amount of uptake. They favour a physico-chemical explanation of the mechanism of vegetable tanning. Physico-chemical aspects of vegetable tanning processes for leather have been comprehensively summarised by E. G. Cockbain<sup>62</sup> (see also Mineral Tannages), who also stresses the importance of the non-electrovalent forces in tannage.

Practical tanning experiments, using as a control in the tanning liquors the ratio of total acid to total salt determined as described by Cheshire *et al.*,<sup>62</sup> have been carried out by R. L. Okell.<sup>64</sup> Quite half of the non-tans in the weaker tan liquors consist of salts, especially calcium, potassium, sodium, and magnesium compounds, and the total acidity (of myrobalan and chestnut liquors of density 1.10) approaches 0.5N. Liquors having a high acid/salt ratio produce a firm leather having a low shrinkage temperature. The chestnut in a commercial sole leather tannage was gradually replaced by mimosa and myrobalan extracts plus sufficient acetic acid to maintain the original acid/salt ratio and the character of the resulting leather was unchanged.

*Chrome Tanning.*—The main reaction in chrome tanning is considered by E. G. Cockbain<sup>62</sup> to consist of co-ordination between CO groups in adjacent collagen main chains with hydroxyl groups of the chromium complex, thereby forming stable cross-linking. The effect of "masking" agents in chrome tanning is attributed to a reduction in the astringency of the chrome liquor, due to the entry of organic acid radicals into the chromium complex weakening the co-ordinating power of the chromium atom for other groups.

Although not usually considered as tanning, the dyeing of leather also involves the combination of the tanned pelt with still more material and is therefore analogous to it. E. G. Cockbain<sup>62</sup> has pointed out that dipole-dipole forces of attraction and probably H-bonds exist between acid and direct dyes and leather. Van der Waals forces of attraction also play a significant part in dyeing. It is also made clear that the penetration of a dye may depend more on the degree of its aggregation in solution than on actual affinity of dye for leather. The degree of aggregation of the tanning molecules has always been a complicating factor in studying tans and tanning.

<sup>61</sup> *J. Chinese Chem. Soc.*, 1944, 11, 86; B., 1945, II, 159.

<sup>62</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 102; B., 1945, II, 255.

<sup>63</sup> R. Hodgson & Sons, and A. Cheshire; B., 1941, II, 406.

<sup>64</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 56; B., 1945, II, 197.



S. G. Shuttleworth<sup>65</sup> has continued to use his conductometric technique for the elucidation of the structure of complex chromium cations. Investigating the possibilities of the "masking" action of neutral salts in chrome tanning he has obtained conductometric titration curves of 33% sulphur dioxide reduced chrome liquors which were "masked" by additions of sodium salts of acetic, formic, and lævulic acids. From the curves he has concluded that the sodium salts of monobasic organic acids displace the sulphate groups in a sulphate chromium complex forming a new complex stable at a dilution of M./5000 and containing no electrovalent groups and that this complex reacts with dilute alkali liberating the sodium salt of the organic acid, and forming a 66 $\frac{2}{3}$ % basic complex which is fully olated and also appears to contain no electrovalent groups.

G. D. McLaughlin and H. R. Wilson,<sup>66</sup> concerned with the thermal behaviour of cationic chrome-tanned leather, have found that with chromium sulphate tannages the shrinkage temperature is a maximum at 66.7—83.3% basicity and with chromium chloride tannages at 100%. With sulphate tannages the shrinkage temperature is a straight-line function of the amount of protein-bound acid. Also, the shrinkage temperature at 100% basicity increases with increasing chromium content and shrinkage temperatures of 127° are obtained even in complete absence of acid radicals. Deamination of skin before tanning does not reduce the thermal resistance of the resulting leather.

K. H. Gustavson<sup>67</sup> has studied solutions of basic chlorides and sulphates of chromium by means of cation and anion interchanging organolites, and has shown that in solutions of extremely basic chromic chlorides, the major part of chromium is present as uncharged molecules. This method of investigation seems to offer promising possibilities in elucidating a number of the problems of chrome tanning.

A. Küntzel and O. Laasted<sup>68</sup> described the manufacture of a soft and fine-feeling chrome leather produced by air oxidation of pelt previously impregnated with a solution of bivalent chromium salt ( $\text{CrSO}_4$ ). The uptake of chromium from solutions of the bivalent salts by pelt depends directly on the concentration (unlike the case of tervalent salts). The bivalent solution itself has no tanning action, but after 12 hours' exposure of dipped pelts to air, tannage is complete. A. Küntzel and H. Kuhtz<sup>69</sup> have critically examined several methods of determining acid in chrome leather.

A patent has been taken out<sup>70</sup> for the preparation of  $\text{Cr}(\text{OH})\text{SO}_4$  solution by a method which allows commercially valuable organic acids

<sup>65</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 3; A., 1945, I, 147.

<sup>66</sup> *J. Amer. Leather Chem. Assoc.*, 1945, 40, 267; B., 1945, II, 326.

<sup>67</sup> *Svensk Kem. Tidskr.*, 1944, 56, 14.

<sup>68</sup> *Collegium*, 1942, 169; B., 1946, II, 145.

<sup>69</sup> *Ibid.*, 217; C., 1946, 24.

<sup>70</sup> L. R. B. Hervey, Assr. to A. D. Little, Inc., U.S.P. 2,178,874; B., 1945, II, 67.



to be made and recovered as by-products. P. S. Briggs<sup>71</sup> has published results of some interesting experiments on the chrome re-tanning (semi-chrome tanning) of previously partly-tanned leather. He has used the formula  $K't = [\text{Cr}]^{-n} - 1$ , where  $K'$  and  $n$  are constants and  $[\text{Cr}]$  is the decimal fraction of the initial chromium content remaining after  $t$  hours, to relate the degree of exhaustion of the chrome tanning bath to the time of tanning, and has obtained good agreement between observed and calculated values over a wide range of tanning conditions.

#### BACTERIOLOGY AND MICROBIOLOGY.

Both in the U.S.A. and Great Britain bacteriology and microbiology are becoming of increased practical importance in the leather industry. Recent work has been concentrated on the investigation of disinfectants for use during manufacturing processes and on leather, leather goods, and used shoes. The microbiological problem has been to find minimum quantities of disinfectants or mixtures of disinfectants which would be toxic to a variety of species of mould and bacteria but non-toxic to human skin. The industrial problem has been to determine the most satisfactory ways of incorporating disinfectants into the leather.

In the U.S.A.<sup>72</sup> the need has been felt for a standard method of measuring the resistance of leather to the growth of fungi and the method used by R. Lollar<sup>73</sup> has been proposed, with a modification. M. Dempsey<sup>74</sup> has recommended the addition of *p*-nitrophenol,  $\beta$ -naphthol, or cresylic acid at one of several stages during the tanning process for the effective disinfection of leather against mould growth, and has also described a method for testing mouldproofness. Finished leather articles can be dealt with by spraying them with 50% aqueous methylated spirit containing either 0.25% of *p*-nitrophenol or 1% of  $\beta$ -naphthol.

Many species of mould and bacteria inhabit army boots and shoes, especially used ones, and H. Greene,<sup>75</sup> continuing his investigations, has isolated 20 species of bacteria and 9 species of mould, including pathogenic types, from used army shoes. He has shown that although formaldehyde vapour effectively sterilises infected leather sample pieces, used shoes need stronger treatment. For them, successive immersion in (a) 1% formaldehyde solution for 5 minutes at 30°, (b) 0.3% soap solution for 5 minutes, (c) 0.5% sodium bisulphite for 2 minutes to remove excess of formaldehyde, (d) a 10% cationic oil emulsion containing 0.5% of pentachlorophenol, is recommended. Patch tests on such treated leather have shown it to be non-toxic.

C. O. Fulton, N. E. Gibbons, and R. L. Moore<sup>76</sup> have also investigated methods of disinfecting salvaged shoes and found phenylmercuric acetate,

<sup>71</sup> *J. Soc. Leather Trades' Chem.*, 1945, **29**, 123; B., 1945, II, 287.

<sup>72</sup> *Phys. Testing Comm. A.L.C.A., J. Amer. Leather Chem. Assoc.*, 1945, **40**, 239.

<sup>73</sup> *Ibid.*, 1944, **39**, 12, 179; B., 1944, II, 299.

<sup>74</sup> *J. Soc. Leather Trades' Chem.*, 1945, **29**, 133; B., 1945, II, 287.

<sup>75</sup> *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 96; B., 1945, II, 198.

<sup>76</sup> *Canad. J. Res.*, 1944, **22**, F, 163; B., 1945, III, 114.



under fat-liquoring conditions, effective in 1 : 100,000 dilution. During the experiment it was found that vegetable-tanned leather had a fungicidal effect on one strain of *Trichophyton gypsum* and two strains of *T. interdigitale*, but not on several strains of common mould contaminants.

J. F. Wagoner<sup>77</sup> has found that the acidity of weak tan liquors can be maintained without loss for 14 days by the addition of 0.04% of  $\beta$ -naphthol. This substance apparently has the property of destroying the acid-consuming organisms without affecting the acid-producing ones.

A. Steigmann<sup>78</sup> has published a rapid bacteriological test for suspected infection in gelatin raw materials and gelatins. H. Anderson<sup>79</sup> has investigated the adaptation of various bacteria to growth in the presence of sodium chloride and has supported G. D. McLaughlin's<sup>80</sup> suggestion that the re-use of salt from hides is to be deprecated. *B. subtilis* and *B. mycoides*, both strongly proteolytic bacteria, succeeded rapidly in adapting themselves to high salt concentrations.

#### PHYSICAL PROPERTIES OF LEATHER.

The chemist who sets out to apply his chemistry to the practical art of leather making soon finds that, whereas considerable chemical effort is needed in acquiring control of the variety of liquors and processes which are needed, the final product has, so far, defied attempts to assess it satisfactorily by chemical means. Leather is judged to be satisfactory or not for a particular purpose mainly by its physical properties, for example, resistance to wear, strength, firmness in some kinds of leather, softness in others, stretchiness in gloves, "leathery" feel. Hence, many chemists have been forced to the borderline of physics, and beyond, to find some means of measuring and recording the results of their practical efforts in the tannery. More and better methods of investigating and evaluating more leather properties and papers announcing results of the effects of tanning processes on the physical properties of leather continue to occupy considerable space in the journals of leather chemists. Many of the existing methods must, of necessity, be empirical in character, but steps have been taken throughout the year to standardise them, after subjection to critical examination.<sup>81</sup> In Germany also,<sup>82</sup> standards for evaluating leather were proposed during the war years.

Before it is possible to draw the proper conclusions from any experiment in which physical tests are applied, unusual forethought in regard to sampling and to the variability of the material under examination is essential. This point is stressed by a most valuable contribution, statistical in nature, from R. B. Hobbs.<sup>83</sup>

<sup>77</sup> *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 222; *B.*, 1945, **II**, 287.

<sup>78</sup> *J.S.C.I.*, 1944, **63**, 288; *C.*, 1945, 32.

<sup>79</sup> *J. Soc. Leather Trades' Chem.*, 1945, **29**, 215; *B.*, 1946, **II**, 26.

<sup>80</sup> *J. Amer. Leather Chem. Assoc.*, 1928, **23**, 300.

<sup>81</sup> *Ibid.*, 1945, **40**, 4, 7, 8, 238, 337, 338, 360. J. W. Harnly and W. P. Parker, *ibid.*, 1945, **II**, 231; *C.*, 1945, 174.

<sup>82</sup> *Collegium*, 1942, 146; *B.*, 1946, **II**, 144.

<sup>83</sup> *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 348.



*Sole Leather.*—The wearing properties under various conditions of sole leather, measured as resistance to abrasion on machines of several different types,<sup>84</sup> have received the attention of a number of workers. In U.S.A., experimental tracks, simulating actual wear but under more drastic than normal civilian conditions, are also in use.<sup>85</sup> R. B. Hobbs and R. A. Kronstadt<sup>86</sup> have tried to correlate resistance to abrasion tests with results of actual wear and have found that some abrasive machines give a better correlation than others. They have also found that there is much loss of extractable grease during wear and have confirmed that good wearing properties are associated with firmness<sup>87</sup> and low water-soluble content.<sup>88</sup> There is still some controversy about the latter factor, however.<sup>89</sup> R. P. Hermoso<sup>90</sup> has studied factors influencing changes in resistance to abrasion of vegetable-tanned sole leather and, whilst unable to find a direct correlation between resistance to abrasion and actual wear, did find a good relationship between these properties in 85% of cases (200 pairs).

R. L. Moore<sup>91</sup> has found that, during wet wear, tannin is stripped from the surface of leather at a rate depending on the pH of the soil solution in contact with the leather and the character of the tannin, resistance to wet wear being closely related to the amount of N./22 calcium hydroxide required to raise the pH of the leather to 7.0. He considers that leather more resistant to hydrolysis is produced by low concentrations of the less astringent tannins and that leather tanned with wattle, hemlock, and the ellagi-tannins is hydrolysed at higher pH value than leather tanned with quebracho or chestnut. He also considers that the increased use of quebracho has materially reduced the wear of present-day sole leather (but no evidence confirming this has appeared in this country). In further studies<sup>92</sup> of the resistance of leather to wear while wet and in contact with different types of soil solutions, the same author has indicated lines on which the processes and materials ordinarily used in producing sole leather may be altered to influence the wear while wet.

The rigidity of sole leather has been studied by P. White and F. G. Caughley,<sup>93</sup> who have found that, under dry conditions, the dominating factors contributing to rigidity are the condition, distribution, and amount of water-soluble matter present; in wet conditions the dominant factor is associated with the amount of material insoluble in water

<sup>84</sup> D. Jordan Lloyd, *J. Soc. Leather Trades' Chem.*, 1939, 23, 461.

<sup>85</sup> W. T. Roddy, *J. Amer. Leather Chem. Assoc.*, 1945, 40, 300; R. L. Moore, *ibid.*, 303; B., 1946, II, 27.

<sup>86</sup> *Ibid.*, 12; B., 1945, II, 198.

<sup>87</sup> G. O. Conabere, *J. Soc. Leather Trades' Chem.*, 1944, 28, 25.

<sup>88</sup> H. Bradley and A. Colin-Russ, *ibid.*, 1927, 11, 329.

<sup>89</sup> *J. Amer. Leather Chem. Assoc.*, 1944, 39, 134.

<sup>90</sup> *Ibid.*, 1945, 40, 169; B., 1945, II, 198.

<sup>91</sup> *Ibid.*, 1944, 39, 243; B., 1944, II, 336.

<sup>92</sup> R. L. Moore, *ibid.*, 1945, 40, 303; B., 1946, II, 27.

<sup>93</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 148; B., 1945, II, 395; C., 1945, 246.



deposited on or between the fibres. P. Chambard<sup>94</sup> has also been studying hardness of sole leather, using measurements of changes in thickness of wet and dry leather under pressure to assess this property.

*Light Leather.*—G. O. Conabere<sup>1</sup> has shown that lines of tension in the raw skins of calf, goat, and sheep still exist in the finished leather and that the fibre weave, also directions of maximum stiffness and tensile strength, and minimum stretch are related to them. Chrome-tanned calf shrinks most in a direction parallel to these lines of tension when raised to the shrinkage temperature.

The chemical characteristics<sup>95</sup> and the inter-relations between these and the microscopical<sup>96</sup> properties of chrome calf upper leather have been described, and F. Stather and H. Herfeld<sup>97</sup> have examined various chrome-tanned ox and calf leathers from the point of view of distribution of values of tensile strength, stretch, and apparent density over the entire areas, and have deduced, from the results obtained, the directions of run of the main fibre bundles. These authors<sup>98</sup> have also published results of long-range tests of the stability of vegetable-tanned leather, some containing up to 50% of added syntans, on storage. After storage of from 3 to 8 years it was found that changes in leather on storage depended more on variations from tannery to tannery than on whether the leather had been tanned with or without the addition of syntans. General changes on storage were decreases in the amounts of extractable grease and water-soluble matter. There were very slight decreases in pH and a moderate increase of the difference figure. The authors were not able to detect any adverse influence on the strength properties.

R. G. Mitton<sup>99</sup> has made a careful examination of several mechanical properties of vegetable-tanned leather fibres, and their changes as alterations in the relative humidity of the surrounding atmosphere cause the amount of moisture held by the fibres to increase or to decrease. Fibres lose moisture on passing from an atmosphere of high relative humidity to a lower one and vice versa, as leather does in bulk, and the author considers that water is absorbed in three ways, strongly bound water amounting to about 2.5% of the dry weight of the fibres, loosely bound water to 20%, and the water described as capillary condensed to several times as much. The loosely bound water is equivalent to an absorption of one or two molecules per residue of the collagen. The rigidity modulus of fibres decreases as the amount of adsorbed water increases. Plastic flow is found to occur at high humidities, but if a fibre is kept under constant load its extension with humidity changes (after an initial plastic extension has occurred) is reversible, and a fibre kept in an atmosphere of constant relative humidity obeys Hooke's law approximately at all

<sup>94</sup> *Doc. Sci. Tech. Ind. Cuir*, 1942, 40; *Chem. Abs.*, 1945, 2665.

<sup>95</sup> E. W. Merry, *J. Soc. Leather Trades' Chem.*, 1945, 29, 223; *B.*, 1946, II, 107.

<sup>96</sup> G. O. Conabere, *ibid.*, 232; *B.*, 1946, II, 107.

<sup>97</sup> *Collegium*, 1942, 1; *B.*, 1946, II, 144.

<sup>98</sup> *Ibid.*, 1943, 210; *B.*, 1946, II, 107.

<sup>99</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 169; *B.*, 1946, II, 26.



extensions up to breaking point. Dry fibres can be heated to at least  $170^{\circ}$  without apparent deterioration and the coefficient of linear expansion of dry fibres is  $22 \times 10^{-6}$  per  $^{\circ}\text{C}$ . The sudden shrinkage characteristic of wet leather does not occur unless the relative humidity approaches 100%.

F. Stather and H. Schöpel<sup>100</sup> have described an apparatus for measuring thermal conductivity of leather with reference to a sheet of standard material (Plexiglass) and find that chrome-tanned leather has a lower thermal conductivity than vegetable-tanned leather.

#### ANALYTICAL METHODS.

*Tannins.*—M. Nierenstein and co-workers have published micro-methods for the estimation of tannins<sup>101</sup> and ellagitannins<sup>102</sup> and also a method of quantitatively precipitating tannins by means of azo-dyes<sup>103</sup> chrysoidine, Bismarck-brown, Congo-red, Arypan-red, Afridol-blue, and Echtgelb, each of which contains a free amino-group. By means of the latter method the number of depsiphore groups<sup>104</sup> may be determined. The micro-method for ellagitannins<sup>102</sup> is stated<sup>105</sup> to estimate 0.25 mg. of tannin with certainty, whilst the elaborated antipyrine method<sup>106</sup> gives uncertain results with 1 mg. and fails with 0.75 mg. of tannin. The micro-method for the determination of tannin is stated to estimate tannin in single leaves after suitable treatment and extraction. C. A. Mitchell<sup>107</sup> has proposed that as the tannin used by Nierenstein<sup>101</sup> as a standard is an exceptional glucose-free tannin, the use of the Lovibond scale or of analytical standardisation (involving determination of pyrogalllic groups) would make the Nierenstein standards more generally available.

J. Haslam, J. S. Wilson, and J. E. Edwards<sup>108</sup> have also described modifications of the method of Berk and Schroeder<sup>109</sup> for the determination of small amounts of tannin in hard water.

G. S. Rich<sup>110</sup> has described a photo-electric method of determining the diffusion of wattle (mimosa) bark tannin solutions. The diffusion constant for mimosa bark tannin is between  $1.84$  and  $1.94 \times 10^6$  cm.<sup>2</sup> per sec., from which a particle size of  $1.84 \times 10^{-7}$  cm. is obtained and a gross molecular weight of 21,300. The American Leather Chemists Association Filter Paper Committee<sup>111</sup> report that filter-paper C.S. & S.,

<sup>100</sup> *Collegium*, 1942, 259; C., 1946, 24.

<sup>101</sup> M. Nierenstein, *Analyst*, 1944, 69, 91; C., 1944, 192.

<sup>102</sup> M. Nierenstein and V. N. Norris, *ibid.*, 241; C., 1944, 192.

<sup>103</sup> R. C. Davies, M. Nierenstein, and C. W. Webster, *ibid.*, 1945, 70, 17; C., 1945, 134.

<sup>104</sup> B., 1943, II, 98.

<sup>105</sup> M. Nierenstein, *Analyst*, 1945, 70, 132; C., 1945, 188.

<sup>106</sup> B., 1934, II, 42.

<sup>107</sup> *Analyst*, 1944, 69, 92; C., 1944, 192.

<sup>108</sup> *J.S.C.I.*, 1944, 63, 179; C., 1944, 187.

<sup>109</sup> B., 1942, I, 394.

<sup>110</sup> *Leather Ind. Res. Inst. (South Africa)*, 1944, *Circ.* 27, 627; B., 1944, II, 336.

<sup>111</sup> J. E. McNutt, *J. Amer. Leather Chem. Assoc.*, 1944, 39, 335; C., 1945, 32.



No. 610 may be used instead of Munktell's No. IF. in the determination of soluble solids in vegetable tanning extracts.

The extraction of leather by water continues to receive attention, and A. Cheshire and C. G. Turner<sup>112</sup> have shown that the amount of soluble matter removed from leather by washing increases with rising temperature, increasing pH, and decreasing surface tension of the solvent. Hence, in the determination of fixed tan by the Wilson-Kern method, the time, temperature, pH, and surface tension of the wash water should be standardised.

A method of determining the amount of acid combined with chromium in the presence of ammonium salts in chrome liquors is given by D. Burton and G. A. Mittler.<sup>113</sup>

Drying animal tissues in an evacuated desiccator at room temperature has been found<sup>114</sup> to be a more reliable method for determining water and fat content of skin than drying in an oven at 100—105°.

The use of selenium as a catalyst in the Kjeldahl method of digestion<sup>115</sup> is of particular importance in leather analysis and the question of whether or not selenium, either alone or when used in combination with other catalysts, brings about a loss of nitrogen has received considerable study. Several workers<sup>116</sup> have found losses under certain conditions, although C. F. Poe and M. I. Nalder<sup>117</sup> found no losses of nitrogen when selenium was used with potassium sulphate and A. E. Beet and D. G. Furzey<sup>118</sup> were satisfied with the catalyst under the conditions described by them. Bradstreet<sup>119</sup> also reported no losses when less than 0.25 g. of selenium was used, either alone or with other catalysts, but did find losses when more than this amount was used. E. Rauterberg and H. Benischke<sup>120</sup> have confirmed after investigating various catalysts that losses of nitrogen were insignificant when moderate amounts of potassium sulphate were used with selenium; they also found no advantage in the use of hydrogen peroxide over the use of copper sulphate.

R. Ganday<sup>121</sup> has described a method for determining *p*-nitrophenol in full chrome leather.

#### MISCELLANEOUS.

Papers and patents<sup>122</sup> dealing with general improvement of furs have

<sup>112</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 86; B., 1945, II, 231; C., 1945, 175.

<sup>113</sup> *Ibid.*, 2; C., 1945, 93.

<sup>114</sup> W. Wynn and J. Haldi, *Amer. J. Physiol.*, 1944, 142, 508; C., 1945, 178.

<sup>115</sup> M. F. Lauro, *J. Ind. Eng. Chem. [Anal.]*, 1931, 3, 401.

<sup>116</sup> C. F. Davis and M. Wise, *Cereal Chem.*, 1933, 10, 488. R. A. Osborne and A. J. Krasnitz, *J. Assoc. Off. Agric. Chem.*, 1934, 17, 339. N. Illarionov and N. A. Szolovjeva, *Z. anal. Chem.*, 1935, 100, 328. R. M. Sandstedt, *Cereal Chem.*, 1932, 9, 156. S. R. Snider and D. A. Coleman, *ibid.*, 1934, 11, 414.

<sup>117</sup> *Ind. Eng. Chem. [Anal.]*, 1935, 7, 189.

<sup>118</sup> *J.S.C.I.*, 1936, 55, 108T.

<sup>119</sup> *Ind. Eng. Chem. [Anal.]*, 1940, 12, 657.

<sup>120</sup> *Bodenk. Pflanzenernähr.*, 1941, 26, 97; C., 1944, 190.

<sup>121</sup> *J. Soc. Leather Trades' Chem.*, 1945, 29, 143; C., 1945, 246.

<sup>122</sup> B.P. 564,316; B., 1944, II, 381. U.S.P. 2,328,236; B., 1945, II, 273. B.P. 569,146; U.S.P. 2,193,637; U.S.P. 2,309,254; B., 1945, II, 273; 1944, II, 337.



appeared, many practical aspects of fur making being given, particularly in regard to dyeing and dressing, by A. Ginzel.<sup>123</sup>

A new technique for separating oils into free oxidised and non-oxidised fatty acids, unsaponifiable matter, combined oxidised fatty acids, and solid and liquid combined fatty acids has been described by D. Burton and G. F. Robertshaw,<sup>124</sup> and the values for various commercial oils recorded. Cod oils for currying should contain about 6% of free fatty acid to assist penetration, but those containing more than 14% are liable to give gummy spues and are more suitable for chamoising than for currying.

The rôle of various sulphated fatty oils in the fatliquoring of chrome leather has been investigated by R. M. Koppenhoefer.<sup>125</sup> The amount of combined oil in treated leathers was found to be directly proportional to the combined sulphur trioxide in the oil. Cod oil showed rather more and castor oil rather less than average penetration. Generally, the marine and animal oils proved superior to the vegetable oils.

During the war the utilisation of waste leather was a matter of importance and several patents dealing with detanning of leather and degradation of leather protein<sup>125</sup> on the one hand, and production of reconstituted leather<sup>126</sup> and laminated leather products<sup>127</sup> on the other, have appeared.

A. Colin-Russ<sup>128</sup> has begun fundamental studies on the degradation of leather protein and has started with a paper on the kinetics of the system chrome leather-hydrogen chloride. The same author has also described the production of dyestuffs from waste leather<sup>129</sup> and has given a formula for making artificial "perspiration" to be used in studies of leather deterioration in use.<sup>130</sup>

<sup>123</sup> *Textilber.*, 1943, **24**, 87, 438; 1944, **25**, 138; B., 1945, II, 19, 109.

<sup>124</sup> *J. Soc. Leather Trades' Chem.*, 1945, **29**, 28; B., 1945, II, 159.

<sup>125</sup> B.P. 568,182; B., 1945, II, 231. B.P. 566,349; B., 1945, II, 127. B.P. 565,969; B., 1945, II, 92.

<sup>126</sup> B.P. 570,250; B., 1945, II, 327.

<sup>127</sup> B.P. 568,602; B., 1945, II, 327.

<sup>128</sup> *J.S.C.I.*, 1944, **63**, 372.

<sup>129</sup> *Chem. Tr. J.*, 1944, Nov. 24.

<sup>130</sup> *J. Hygiene*, 1945, **44**, 53; C., 1945, 246.



# AGRICULTURE AND HORTICULTURE.

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THE distribution of agricultural literature during the period under consideration is still of necessity restricted by war conditions. Much doubtless fails to come to hand: a great deal arrives very irregularly. Any attempt to deal with the year's publications alone would yield a very incomplete review and would probably fail to record the logical sequence of development. It is preferable, once again, to consider selected subjects using appropriate literature reaching us during the past two or three years. Among the subjects the analysis of soils and of fertilisers, the every-day tool of the profession, becomes of even greater significance as the increasing burden of routine work falls on thinning ranks. It is inevitable that current investigations are largely concerned with accelerating established methods adopted in more leisurely days. In this connexion the separate publication of grouped analytical abstracts by the Bureau of Abstracts has proved a welcome innovation. Continued interest in the physical properties of soils, especially as related to their water economy and to cropping, demonstrates an ever widening appreciation of the economic aspects of this subject.

Among horticultural interests the practical application of the varied effects of growth-substances on plants continues to provoke widespread research. Recent investigations of the complicated effects of light on plant growth have reached a stage at which new practical implications are becoming apparent. Controlled supplementary lighting and shading in horticultural work is attracting much attention and some consideration of the subject in this Report seems desirable.

## LABORATORY EXAMINATION OF SOILS.

### *Chemical Analysis.*

*Nitrogen.*—The chemical examination of soils in general is either directed towards advisory work in connexion with cropping and manurial treatments or is applied to specific investigational purposes of a more detailed or more fundamental kind. In the former category the more or less standardised macro-methods for assessing the nitrogen, potassium, phosphate, lime, etc. contents are well established and in recent years have been subject to little change beyond minor variations in laboratory technique. Thus, in the case of the determination of total nitrogen in soils almost the only modifications recorded have concerned the catalyst used in the Kjeldahl method. According to various authors the enhanced rate of destruction of organic matter attained by the use of selenium



catalysts may be attended by additional risk of loss of nitrogen in the process. This applies to various selenates, which when used in conjunction with mercuric oxide are more effective than elementary selenium in the digestion of protein material<sup>1</sup> but may incur undue loss of nitrogen. In soil analysis, however, there seems fairly general agreement that elementary selenium without mercury gives satisfactory results, as was shown earlier by E. Rauterberg and H. Benischke,<sup>2</sup> provided excessive amounts of potassium sulphate in the digestion mixture are avoided. The use of hydrogen peroxide, as advocated by many workers, is now stated to offer no advantage over that of copper sulphate. E. M. Emmert<sup>3</sup> adopts the sulphuric acid-sodium chlorate method in a small-scale technique, using 0.1-g. samples, provision being made in an intermediate stage for the conversion of amide-nitrogen into glycine by additions of monochloroacetic acid and sodium hydroxide. After a second treatment with acid-chlorate the nitrate in the final digest is determined by the phenoldisulphonic acid method. In a more detailed scheme of analysis of soil-nitrogen (total, ammoniacal, nitrate, nitrite) A. L. Prince<sup>4</sup> reverts to the use of mercury as catalyst in the Kjeldahl digestion, and determines ammonia-nitrogen in the N-sodium chloride leachate of soils by distillation with magnesium oxide, and nitrate and nitrite colorimetrically by the phenoldisulphonic acid and  $\alpha$ -naphthylamine methods, respectively, in aqueous soil leachates. An interesting elaboration of the  $\alpha$ -naphthylamine-sulphanilic acid process for determining nitrite involves the use of sulphanilamide and *N*-1-naphthylethylenediamine dihydrochloride.

*Phosphate.*—Recent work on methods for determining the total phosphate in soil is largely aimed at speeding-up the process by adapting the popular molybdenum-blue technique in substitution for the standard phosphomolybdate precipitation method. This necessitates in most cases the preliminary removal of organic matter, which is effected by replacing the former hydrochloric acid extraction by an oxidative digestion process, for which perchloric acid appears to be suitable. W. R. Shelton and H. J. Harper<sup>5</sup> utilise 70—72% perchloric acid for this purpose and subsequently extract the phosphate with water. After neutralising the extract with aqueous ammonia (2:6-dinitrophenol indicator), phosphate is determined by the molybdenum-blue method using hydrazine sulphate as reducing agent. A similar technique is described by R. H. Bray and L. T. Kurtz.<sup>6</sup> With certain red soils of Ceylon the standard methods have long been found to present difficulties, and in this case J. G. Shrikhande<sup>7</sup> describes a suitable process involving preliminary digestion

<sup>1</sup> R. S. Dalrymple and G. B. King, *Ind. Eng. Chem. [Anal.]*, 1945, 17, 403; C., 1945, 273.

<sup>2</sup> *Bodenk. Pflanzenernähr.*, 1941, 26, 97; C., 1944, 190.

<sup>3</sup> *Soil Sci.*, 1944, 58, 205; C., 1945, 54.

<sup>4</sup> *Ibid.*, 1945, 59, 47; C., 1945, 271.

<sup>5</sup> *Iowa State Coll. J. Sci.*, 1941, 15, 403; B., 1943, III, 45.

<sup>6</sup> *Soil Sci.*, 1945, 59, 39; C., 1945, 271.

<sup>7</sup> *J. Agric. Sci.*, 1942, 32, 406; B., 1943, III, 30.



with sulphuric acid using a selenium catalyst; a single digested sample can thus be used for the determination of total phosphorus and nitrogen.

Bray and Kurtz<sup>6</sup> also record a method for differentiating between different forms of phosphorus in soils. It is assumed that phosphate readily available to plants is either soluble in 0.1N-hydrochloric acid or is adsorbed by soil colloids and is extractable by 0.03N-ammonium fluoride. Separate extractions of soil samples by these two reagents, or by a mixed solution, if only "available phosphate" in general terms is required, are followed by colorimetric determination of phosphate by the molybdenum-blue method. Organic forms of phosphorus are regarded as convertible into phosphate by treatment of the soil with hydrogen peroxide and are represented as the difference between the recorded values for "available" (acid-soluble + adsorbed) phosphate obtained with and without the use of hydrogen peroxide.

Another interesting investigation relating to the determination of available phosphate in soil is that of L. E. Ensminger and H. W. E. Larson.<sup>8</sup> It is shown that the proportion of soil-phosphate which is soluble in aqueous carbon dioxide is related to the response of the soils to phosphatic fertilisers. This response, however, is dependent on the calcium carbonate content of the soils (if less than 2%), being least in those containing 0.5—1.0% of calcium carbonate. High values for phosphate soluble in aqueous carbon dioxide are found in soils of such ranges of calcium carbonate content as are associated with low response to fertilisers. This investigation provides a new angle of approach to the problem of determining available phosphate in soil and possibly to that of availability in general. An earlier paper by A. Schönfeld and E. Dömötör<sup>9</sup> describes a method for assessing the phosphate requirement of soils which is presumably based on a somewhat similar principle. The process depends on a determination of the calcium carbonate content by neutralisation with N-nitric acid and of the amount of phosphate soluble in 0.01N-nitric acid. With these values and the aid of a series of limiting values characteristic of soil types in respect of pH and calcium carbonate and reference to the nature of the crop, the phosphate requirement of the soil may be estimated. By this method agreement with field observations is recorded in over 80% of the soils examined.

*"Rapid" Methods.*—The general tendency towards the speeding-up of these essentially macro-methods by replacing them by the so-called "rapid" or micro-methods referred to in an earlier Report<sup>10</sup> has been due in no small degree to the ever-increasing pressure of routine advisory work. This necessitates close investigation of micro-methods and the establishment of techniques which in general yield data of appropriate accuracy and reproducibility in a wide range of soil types and which are subject to the minimum influence of the "personal factor." L. D. Bauer

<sup>6</sup> *Soil Sci.*, 1944, **58**, 253; B., 1945, III, 54.

<sup>9</sup> *Bödenk. Pflanzenernähr.*, 1941, **25**, 178; C., 1944, 40.

<sup>10</sup> *Ann. Repts.*, 1941, **26**, 369.



and F. H. Brüner<sup>11</sup> discussing this point suggest that unsatisfactory results sometimes obtained by the use of "rapid" methods are due to insufficient specificity of the tests used, to adoption of methods not generally applicable to widely different soil types, to use of a single extractant for all soil nutrients, and (a significant point) to difficulties of interpretation of the analytical data obtained. M. Peech and L. English<sup>12</sup> also criticise commonly used "rapid" methods which are subject to error in presence of extraneous ions which may be present or arise in the course of analysis in unduly different proportions in diverse types of soil. With this in view these authors introduce modifications into existing methods for determining sodium, potassium, calcium, magnesium, manganese, aluminium, iron, phosphate, ammonia, and nitrate, on a micro-scale. J. Tinsley and N. H. Pizer<sup>13</sup> have extended their examination of the Morgan system of rapid testing of soils and record an effective modification of the cobaltinitrite method for potassium. The interpretation of chemical data in advisory work is a matter of great importance and a series of papers by N. H. Pizer<sup>14</sup> affords an insight into the general problem; the author deals not only with the more commonly occurring question of nitrogen, potash, and phosphate manuring and liming, but also with deficiency of secondary nutrients, with methods of sampling (especially in grassland), and with the treatment or reclamation of sea-flooded land.

#### *Evaluation of Nutrient Status of Soils by Plant Analysis.*

The chemical analysis of soils has established itself over a period of years as a normally safe basis for the assessment of fertiliser requirements; nevertheless the methods employed are of necessity empirical in respect of their interpretation. In more fundamental investigations an empirical basis is often a source of weakness or of misdirection, and many workers who are concerned with the nutrient status of soils show a preference for the growing plant rather than a chemical solution as an extractant of nutrient matter from the soil. Moreover, plant analysis offers the better means of studying nutrient conditions at intervals while the crop is actually growing and may become a valuable aid in the effectual use of supplementary fertiliser dressings applicable to the growing crop. It is clear, however, that the two lines of approach to nutritional problems are not strictly comparable and the choice of method is in many ways dependent on the nature of the problem in hand.

Much attention has been given to methods of plant analysis as a means of studying soil conditions since Lagatu and Maume first developed their system of "leaf diagnosis."<sup>15</sup> As generally applied, such methods depend on the comparison of the percentage of nutrients in particular plant parts (leaves, stem sections, petioles) at corresponding stages of physiological

<sup>11</sup> *Missouri Agric. Exp. Sta.*, 1939, *Bull.* 404; C., 1944, 188.

<sup>12</sup> *Soil Sci.*, 1944, 57, 167; C., 1944, 187.

<sup>13</sup> *J.S.C.I.*, 1945, 64, 182; C., 1945, 189. See also *Ann. Repts.*, 1941, 26, 369.

<sup>14</sup> *J. Min. Agric.*, 1945, 52, 164, 205, 270, 315; B., 1945, III, 238; C., 1945, 270.

<sup>15</sup> *Ann. Repts.*, 1941, 26, 371.



development. The earlier the stage of growth at which satisfactory analyses can be made the more complete is the picture of the nutrient status of the soil thus obtained. It is on this basis that much recent research on these methods has been carried out. For example, E. M. Emmert<sup>16</sup> in a study of the nutrition of the tomato determines the optimum proportions of soluble nitrogen and phosphorus in the lower green petioles of the plants at various growth stages up to the commencement of ripening of the fruit and argues that divergences between actual and optimal values reflect deficiencies in soil nutrient content or inadequacies in fertilisers applied. Similarly A. Ulrich<sup>17</sup> reports that the potassium content of petioles of the grape is directly related to the manurial treatment and to the yield. It is claimed that the potassium status is demonstrated more accurately by petiole analysis than by that of leaves or by direct analysis of the soil. A similar conclusion is reached<sup>18</sup> in respect of the nitrogen status as indicated by the nitrate content of the petioles; it is shown that nitrate is a more suitable basis of measurement than is the soluble, insoluble, or total nitrogen. In another publication<sup>19</sup> the same author discusses, theoretically, the use of plant analysis as an index of the level of nutrient supply in the soil and comments, in regard to potassium, on the importance of establishing reliable critical values for the petiole content.

In an examination of sugar-beet petioles as a measure of the available phosphate and nitrate in soil, R. J. Brown<sup>20</sup> finds that closest correlation is obtained if the petiole of the youngest mature leaf is examined. It is stated, however, that in applying the method to field crops a sample of four hundred petioles is necessary to ensure results of suitable accuracy (probability 19:1). In blackberry and raspberry canes, in which an increased supply of potassium to the roots is associated with improved growth, larger yields, and a higher percentage of potassium in the leaves, H. E. Clark and W. L. Powers<sup>21</sup> have established the critical and optimum potassium contents of leaves and have utilised these values in determining the fertiliser requirements of the canes. According to H. Lundegårdh<sup>22</sup> the available nitrogen, potassium, phosphate, and calcium in soil may be ascertained from the proportion of these nutrients present in plant leaves at the flowering stage.

These methods of determining fertiliser requirements based essentially on correlating the soil supply of an individual element and the proportion of that element in a particular plant organ may be open to misinterpretation unless other factors are taken into consideration. Thus the nitrogen

<sup>16</sup> *Proc. Amer. Soc. Hort. Sci.*, 1940, **37**, 272; 1941, **38**, 621; A., 1943, III, 699; B., 1943, III, 173.

<sup>17</sup> *Ibid.*, 1942, **41**, 204; B., 1943, III, 205.

<sup>18</sup> A. Ulrich, *ibid.*, 213; A., 1943, III, 613.

<sup>19</sup> *Soil Sci.*, 1943, **55**, 101; B., 1943, III, 201.

<sup>20</sup> *Ibid.*, **56**, 213; B., 1944, III, 82.

<sup>21</sup> *Plant Physiol.*, 1945, **20**, 51; B., 1945, III, 160.

<sup>22</sup> *Nature*, 1943, **151**, 310; B., 1943, III, 118.



content of apple leaves is shown by D. E. H. Frear and R. D. Anthony<sup>23</sup> to be correlated positively with the supply of fertiliser nitrogen but the absolute relationship changes with the period of the year. J. F. Harrington,<sup>24</sup> utilising analyses of extracts of plant tissues (notably conductive tissue), finds these to be related to soil nutrient supplies in a manner which is dependent on soil type. Manurial requirements therefore can be determined only by comparison of data obtained from the individual type of soil. This point may be clarified by further investigation, but for the moment it imposes serious limitations on the application of plant diagnostic methods.

In following up earlier work previously referred to in these Reports,<sup>25</sup> W. Thomas and W. B. Mack<sup>26</sup> develop the system originated by Lagatu and Maume by which the balance of nitrogen, phosphate, and potassium in leaves, *e.g.*, third leaf of maize or fourth leaf of potato, is brought into consideration as well as the actual amounts present. The "N-P-K equilibria" are expressed graphically with the aid of tri-linear co-ordinates. It would now appear also that a "Ca-Mg-K equilibrium" may serve to characterise the nutrient status of soils in greater detail. In a more recent paper<sup>27</sup> the same authors apply this system to an examination of the influence of weather conditions and of liming on the nutrition of maize under various manurial treatments. It is shown that the characteristics of N-P-K nutrition, represented graphically as the locus of N-P-K equilibria, are similar at all ranges of soil-pH examined and under varied climatic conditions although crop yields may differ considerably. The Ca-Mg-K equilibria in these experiments reflect the applications of lime. On somewhat similar lines C. E. Beauchamp<sup>28</sup> records an examination of potato nutrition employing alcoholic extracts of leaf samples taken 52 days after planting. Interrelationships between the amounts of fertiliser materials applied and the percentage of nitrogen, potassium, phosphate, calcium, and magnesium in the extracts are established. The percentage of total nutrients in the extracts is directly related to the quantity of fertiliser given.

## BASE EXCHANGE IN SOILS.

### *Laboratory Determination.*

Among methods for determining the exchangeable base content and the exchange capacity of soils, those involving leaching with ammonium acetate solution still seem to find most favour. The original method has been accelerated by the use of smaller samples and by the adaptation of colorimetric and other micro- or semi-micro-methods to the analysis of the

<sup>23</sup> *Proc. Amer. Soc. Hort. Sci.*, 1943, **42**, 115; B., 1945, III, 5.

<sup>24</sup> *Ibid.*, 1944, **45**, 313; B., 1945, III, 161.

<sup>25</sup> *Ann. Repts.*, 1941, **26**, 371.

<sup>26</sup> *Plant Physiol.*, 1938, **13**, 677; 1939, **14**, 75, 699; B., 1944, III, 84, 85; A., 1944, III, 309. *Proc. Amer. Soc. Hort. Sci.*, 1939, **37**, 253; B., 1943, III, 198.

<sup>27</sup> *Soil Sci.*, 1943, **56**, 197; B., 1944, III, 85.

<sup>28</sup> *Plant Physiol.*, 1940, **15**, 485; A., 1944, III, 82.



leachates. The excess of ammonium acetate in the leached soil is commonly removed rapidly by washing with alcohol, and adsorbed ammonia in the residual material is liberated by alkali or neutral salts and determined by distillation, thus giving a value for the exchange capacity. Details of such a procedure are given by M. Peech<sup>29</sup> and a very similar technique is described by C. J. Schollenberger and R. H. Simon<sup>30</sup>; in this latter method the data are further supplemented by a determination of exchangeable hydrogen by electrometric titration. In a semi-micro-method for ascertaining exchange capacities described by C. Cantino<sup>31</sup> the treatment with N-ammonium acetate is carried out in centrifuge tubes at 60—70°. After centrifugal separation of the supernatant liquor the treatment is repeated until all calcium is displaced from the soil. Excess of ammonium acetate is removed by methyl alcohol, and ammonia in the residue determined by distillation with magnesium oxide. A further process for determining the exchangeable base content of soils is advanced by C. Peng and T. S. Chu.<sup>32</sup> The sample is extracted for nine hours in a Soxhlet apparatus with 0.1N-acetic acid. The final extract is evaporated to dryness and the residue is ignited, the mixed oxides and carbonates of the extracted bases being determined by titration. By controlling the rate of siphoning during the extraction at four to five times per hour it is found that the temperature of the liquid actually in contact with the soil at no time exceeds 75°.

A variation of this procedure involves the determination of exchangeable hydrogen by treatment of the soil sample with successive portions of N-ammonium acetate followed by determinations of the resultant pH by means of the glass electrode. The total exchangeable base content is also determined electrometrically using acetic acid in place of ammonium acetate. The standards of comparison for the two determinations are direct pH-titration curves of ammonium acetate and acetic acid respectively. I. C. Brown,<sup>33</sup> who develops this method, finds that the results obtained agree well with those of methods in more general use but which are considerably slower in operation.

A somewhat different method is described by E. P. Netto,<sup>34</sup> in which replaceable aluminium is determined by twice percolating the oven-dried (110°) soil with N-potassium chloride and titrating the leachate with sodium hydroxide using phenolphthalein indicator. By a similar treatment of a second sample with N-calcium acetate and titration of the leachate a value is obtained for the exchangeable hydrogen by calculation according to the Vageler formula. The degree of unsaturation, i.e., the  $(T - S)$  value, is represented as the sum of the exchangeable hydrogen + exchangeable aluminium.

<sup>29</sup> *Soil Sci.*, 1945, **59**, 25; C., 1945, 271.

<sup>30</sup> *Ibid.*, 13; C., 1945, 271.

<sup>31</sup> *Ibid.*, 1944, **57**, 399; C., 1945, 54.

<sup>32</sup> *Ibid.*, **58**, 205; C., 1945, 54.

<sup>33</sup> *Ibid.*, 1943, **56**, 353; C., 1944, 89.

<sup>34</sup> *Rev. Brasil. Quím.*, 1943, **16**, 327; C., 1944, 130.



On a somewhat different basis G. Austerweil<sup>35</sup> suggests a means of ascertaining the exchange capacity of soils by a successive extraction process. Assuming that the process of displacement of ions is a function of ion mobility represented as the exchange coefficient, it can be expressed as the sum of a geometric series. Hence if two terms of the series can be evaluated experimentally the sum of the series may be calculated. The determination of ionic concentrations at two stages of equilibrium in a series of successive displacements provides the necessary data. In base-exchange studies of alkali and saline soils the difficulty of distinguishing between exchangeable and free salt bases is well known. Removal of free salts by washing with aqueous alcohol, the method adopted by many workers, sometimes produces variable results. According to M. Y. Shawarbi and A. G. Pollard<sup>36</sup> the concentration of alcohol used should not be less than 70% if removal of adsorbed sodium is to be avoided and removal of free salt completed with the minimum of leaching.

#### *Some General Considerations of Base Exchange.*

Publications relating to more general aspects of base exchange have been somewhat limited during the past few years. An interesting study of the part played by hydrogen and aluminium ions in the exchange complex, especially in relation to soil acidity, is reported by J. N. Mukherjee and co-workers. It is shown, for example,<sup>37</sup> that the treatment of hydrogen-clays with neutral salt solutions results in the displacement of both hydrogen and aluminium in the complex by the added cations, except in the case of very small concentrations of alkali or alkaline-earth salts, when only hydrogen is displaced. In a subsequent paper B. Chatterjee and M. Paul<sup>38</sup> indicate that both hydrogen and aluminium are present on the surface of the hydrogen-clay particle and that addition of neutral salt results in displacement of these ions partly into the intermicellar liquid but not necessarily entirely free from the influence of the clay particle, and partly into the free supernatant liquid, the extent of the latter form of displacement increasing progressively with the concentration of neutral salt added. This process is probably accompanied by a transformation of aluminium hydroxide into an active condition. The relative proportions of hydrogen and aluminium ions displaced therefore depend on the nature and concentration of the displacing cations. Thus barium chloride displaces more aluminium from the complex than does hydrochloric acid at the same pH level.<sup>39</sup> These observations accord with others reported in another publication<sup>40</sup> on the total exchange capacity of a hydrogen-clay as determined by titration with bases.

<sup>35</sup> *Compt. rend.*, 1941, 213, 505; B., 1943, III, 4.

<sup>36</sup> *J.S.C.I.*, 1945, 64, 31; C., 1945, 128.

<sup>37</sup> J. N. Mukherjee and R. P. Mitra, *Indian J. Agric. Sci.*, 1942, 12, 433; B., 1943, III, 117.

<sup>38</sup> *Ibid.*, 13; B., 1945, III, 34.

<sup>39</sup> J. N. Mukherjee and B. Chatterjee, *ibid.*, 105; B., 1945, III, 34.

<sup>40</sup> J. N. Mukherjee, R. P. Mitra, B. Chatterjee, and S. K. Mukherjee, *ibid.*, 86; B., 1945, III, 34.



Values obtained vary with the base used in the descending order : calcium, barium, sodium in the absence of salts and barium, calcium, sodium in their presence.

The somewhat vexed question as to whether the so-called "free sesquioxides" in soil are indeed free agents or whether they form an essential part of the exchange complex receives further attention from this same group of workers. Removal of the sesquioxides from hydrogen-clays by Tamm's or Mattson's reagent causes an increased displacement of aluminium by barium chloride,<sup>41</sup> an apparent decrease in exchange capacity, and a modification in the titration curve indicating fundamental changes in the exchange complex. This suggests that the "free" sesquioxides are probably an essential part of the complex and exist in some form of equilibrium with the actual clay particle. In another publication<sup>42</sup> it is shown that diminution in particle size in sub-fractions of hydrogen-clays is associated with an increase in aluminium oxide and a corresponding decrease in ferric oxide and silica contents, but also with a rapid increase in exchange capacity and free hydrogen ion per unit weight. The forms of the titration curves were similar throughout the range of sub-fractions. This apparent gradation of exchange properties according to the size of the particle is probably related to an observation made by J. Clarens and J. Lacroix<sup>43</sup> that the displacement of calcium from soil by added potassium (as nitrate) occurs in successive steps in accordance with a general equation in which the "constants" vary step by step.

Base-exchange properties of soil fractions greater in size than the normal clay have been noted from time to time. J. Gollan, jun. and M. R. Codoni<sup>44</sup> find that this property is limited to soil particles having a mean diameter below  $2 \times 10^{-4}$  cm. and that an exchange capacity is exhibited by larger particles only if they include smaller aggregates. On the other hand, R. Kunin and W. R. Robbins<sup>45</sup> report on exchangeable calcium held by clay, silt, and sand fractions, all of which provide calcium equally available to plants.

The significance of exchangeable bases in plant nutrition receives further attention from R. H. Bray,<sup>46</sup> who establishes a direct relationship between the ability of soils to furnish potassium for crops and the exchangeable potassium content of the soils. Under appropriate experimental conditions the exchangeable potassium-crop yield relationship may be represented as a modified Mitscherlich growth equation in which the "effect factor,"  $c$ , is constant for wide ranges of soil types but changes with the nature of the crop under examination.

<sup>41</sup> J. N. Mukherjee, R. P. Mitra, and S. Bannerjee, *Indian J. Agric. Sci.*, 1942, 12, 303; B., 1945, III, 34.

<sup>42</sup> J. N. Mukherjee, R. P. Mitra, and S. K. Chakravorty, *ibid.*, 291; B., 1945, III, 34.

<sup>43</sup> *Compt. rend.*, 1940, 210, 787; B., 1945, III, 217.

<sup>44</sup> *Anal. Asoc. Quím. Argentina*, 1942, 30, 146; B., 1944, III, 221.

<sup>45</sup> *Soil Sci.*, 1944, 57, 137; B., 1944, III, 174.

<sup>46</sup> *Ibid.*, 58, 305; B., 1945, III, 54.



An interesting illustration of the influence of exchangeable bases on the physical properties of soils is advanced by M. R. Nayar and K. P. Shukla,<sup>47</sup> who show that the rate of percolation of water through soils is dependent on the size of the exchangeable ions in the colloid complex. For soils saturated with single bases the relationship is expressed by the equation  $P = \lambda e^{\mu r}$  ( $P$  = rate of percolation,  $r$  = ionic radius, and  $\lambda$  and  $\mu$  are constants for bases of the same valency).

#### RECENT WORK ON FERTILISER ANALYSIS.

*Phosphate.*—The somewhat tedious standard procedure of citric acid or citrate extraction of available phosphate from fertilisers and the subsequent determination of the extracted phosphate has long invited modification but little has been achieved in this direction without sacrifice of accuracy. P. Lederle<sup>48</sup> avoids the final ignition of the magnesium ammonium phosphate precipitate, which he weighs directly after washing with acetone and drying in a vacuum desiccator for ten minutes. This process is applicable to citric acid extracts of basic slag, a special conversion factor for calculating the amount of phosphate present being necessary. F. A. Uhl,<sup>49</sup> utilising this method, records that results obtained agree within 0.3% with those of the standard method. The direct precipitation of phosphate from citric acid extracts of fertilisers by magnesia mixture had earlier<sup>50</sup> been shown to yield satisfactory results.

The complicated problem of the solubility of fertiliser phosphates in 2% citric acid receives some clarification from an investigation of P. Martens.<sup>51</sup> This relates to the influence of calcium citrate, produced during the extraction, on the amount of phosphate removed. It is shown that the rate of increase in solubility of the citrate is a linear function of the concentration of free acid present and is increased by the presence of carbon dioxide. The solubility of bone and rock phosphates falls rapidly with increase in the amount of calcium citrate in solution, whereas that of basic slag remains almost unchanged. It is possible to differentiate different forms of phosphate fertiliser or to detect admixture of different forms by observing the solubilities in 2% citric acid, in a similar solution saturated with calcium citrate, and in aqueous ammonium citrate.

A number of workers have sought to shorten the analysis of phosphate fertilisers by adopting the colorimetric method in spite of the attendant risks involved in the use of small samples or small aliquots. It seems possible that the molybdivanadophosphoric method of R. E. Kitson and M. G. Mellon<sup>52</sup> may be serviceable for this purpose.

<sup>47</sup> *Current Sci.*, 1943, 12, 206; B., 1944, III, 2.

<sup>48</sup> *Z. anal. Chem.*, 1941, 121, 241; A., 1943, I, 284.

<sup>49</sup> *Ibid.*, 122, 398; C., 1944, 10.

<sup>50</sup> U. Stolzenberg, *Bodenk. Pflanzenernähr.*, 1941, 26, 124; C., 1944, 188.

<sup>51</sup> *Z. anal. Chem.*, 1943, 125, 245; C., 1944, 188.

<sup>52</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 379; C., 1944, 158.



T. L. Ogier<sup>53</sup> and G. S. Fraps<sup>54</sup> draw attention to a source of inaccuracy arising through the dissolution in hydrochloric acid of phosphates containing fluorine for the determination of total phosphate by the A.O.A.C. method. The amount of etching of graduated flasks caused by liberated hydrofluoric acid is considerable and in tests made, the accuracy of graduation was affected beyond the tolerance limit (0.2 ml. in 200 ml.) in 5 cases out of 19 examined.

*Potassium.*—Recent modifications of the standard process of analysis of potash fertilisers include that of P. M. Shuey<sup>55</sup> for dealing with mixed fertilisers free from ammonia and organic matter. From such materials potassium salts are extracted with boiling water, iron, aluminium, and calcium are precipitated by a mixture of sodium phosphate and hydroxide, and potassium is determined in the filtrate by the U.S. official platinichloride method. For fertilisers containing ammonia and/or organic matter the method proposed by A. B. Joy<sup>56</sup> avoids ignition of the sample with the risk of loss of potassium. The aqueous extract of the sample is boiled with a mixture of nitric and sulphuric acids and sodium chlorate to destroy organic matter, including urea and cyanamide, prior to the customary procedure for potassium. For samples containing ammonia but no organic matter, the aqueous extract is boiled with saturated ammonium oxalate solution and a filtered aliquot is boiled with sodium hydroxide before the usual precipitation of potassium platinichloride.

In an examination of methods of analysis of fertilisers G. S. Fraps<sup>47</sup> notes that ignition of samples in porcelain dishes tends to cause high results in determinations of potassium. Collaborative work on the A.O.A.C. platinichloride method for potassium is reported by O. W. Ford.<sup>57</sup>

*Nitrogen.*—In connexion with the analysis of nitrogenous fertilisers A. L. Prince<sup>58</sup> reports unfavourably on the proposed use of a ferric sulphate-potassium dihydrogen phosphate mixture for accelerating the Kjeldahl digestion process. According to K. Timofeiuk<sup>59</sup> the formaldehyde method is applicable to the determination of ammonia in mixed fertilisers containing phosphate if the latter is previously removed by treatment with the calcium chloride, followed by sodium hydroxide (to produce pH 8–10) and then by ferric chloride.

The laboratory determination of the availability of organic nitrogen in fertilisers is investigated by E. J. Robins and F. E. Bear.<sup>60</sup> By comparison with pot-culture trials and nitrification tests the satisfactory nature of the carbon/nitrogen ratio as a measure of availability is

<sup>53</sup> *J. Assoc. Off. Agric. Chem.*, 1943, **26**, 196; B., 1943, III, 166.

<sup>54</sup> *Ibid.*, 53; B., 1943, III, 166.

<sup>55</sup> *Ind. Eng. Chem. [Anal.]*, 1943, **15**, 633; C., 1944, 40.

<sup>56</sup> *Ibid.*, 1944, **16**, 383; C., 1944, 188.

<sup>57</sup> *J. Assoc. Off. Agric. Chem.*, 1943, **26**, 59; B., 1943, III, 166.

<sup>58</sup> *Ibid.*, 54; B., 1943, III, 166.

<sup>59</sup> *Zavod. Lab.*, 1939, **8**, 101; B., 1943, III, 199.

<sup>60</sup> *Soil Sci.*, 1942, **54**, 411; B., 1943, III, 198.



established in a wide range of materials. Carbon is determined by the permanganate method for this purpose. In the case of some highly lignified materials the lignin-carbon is omitted from the calculation of the carbon/nitrogen ratio.

*Hygroscopicity.*—The hygroscopicity of fertilisers, an important factor in their storage quality and subsequent ease of drilling, seems likely to demand increasing attention and its determination may well become a matter of routine in fertiliser examination. A method of assessing storage quality from this point of view is established by J. Y. Yee.<sup>61</sup> It is based on the consideration of relative humidity-moisture content curves and appropriate apparatus is described. In another paper Yee with R. O. E. Davies<sup>62</sup> give details of a more elaborate apparatus in which humid air is circulated through a chamber in which the samples are exposed. Equilibrium is thereby attained much more quickly than in the more usual "static" forms of apparatus.

#### WATER RELATIONSHIPS OF SOILS AND CROPS.

The examination of physical properties of soils is largely directed towards several practical objectives. These may be roughly classified as (a) properties relating to the ability of soils to store water and deliver it to the plant, (b) properties concerned in the texture of soil and having a bearing on the ease of cultivation or of penetration by plant roots, (c) properties affecting aëration and therefore fertility and cropping [normally similar to (a) above], and (d) properties of importance in engineering and constructional work, e.g., roads, building, etc. Of the literature coming to hand since this subject was last dealt with in these Reports,<sup>63</sup> a large proportion has reference to the water relationships of soils, especially in respect of crop growth.

#### *Water Capacity of Soils and Availability to Plants.*

Apart from the special problems of irrigation and of those soils in which the water table is very near the surface, the complete picture of the water status of a normal soil must include consideration of the fate of rainwater falling on the surface, of what proportion runs off without entering the soil mass, of the amount which penetrates deeply into the subsoil, and of that which may ultimately be utilised by crops. Obviously all the points are influenced not only by the total rainfall but also by its distribution through the year, by meteorological conditions between periods of rain, by cropping conditions, and many other factors. An attempt to correlate meteorological records and the conservation of water in soil is recorded by W. J. Staple and J. J. Lehane.<sup>64</sup> On the basis that drainage from surface to sub-surface layers in soil occurs only when the field

<sup>61</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 367; C., 1944, 188.

<sup>62</sup> *J. Assoc. Off. Agric. Chem.*, 1944, **27**, 273; C., 1945, 55.

<sup>63</sup> *Ann. Repts.*, 1942, **27**, 367.

<sup>64</sup> *Soil Sci.*, 1944, **58**, 177; B., 1945, III, 53.



capacity of the surface layer is exceeded, that the field capacity of the soils examined is represented by a volume equivalent to 0.8 inch of rain, and that "removable" water may be calculated from evaporation curves, these authors assess the water storage of soil over a 20-year period. This is shown to be in reasonably close agreement with actual field observations. The importance of day-to-day studies of climatic conditions in establishing a satisfactory record of the water relationships of a soil is illustrated by some observations of J. H. R. Coutts<sup>65</sup> on some South African soils. For example, moderate rainfall in August—September seldom penetrates more than 2 inches below the surface and penetration to 9 inches occurs only with continuous rainfall of 1 inch daily. The reverse conditions also yield unexpected data. Thus during summer conditions drying to the extent of reaching the wilting point proceeded to a depth of 8 inches in a week and to 20 inches in 5—7 weeks. In winter the drying rate is two or three times slower. These data apply to one particular soil (heavy type) and to a specific set of conditions, but, nevertheless, serve to emphasise the value of observations of a kind which, although of obvious bearing, are frequently overlooked.

Measurements of the pore space and permeability of soils are naturally concerned with problems of infiltration rates and drainage. Important practical difficulties in obtaining data arise in the making of observations on undisturbed soil samples or, alternatively, on the correlation of values obtained from disturbed samples with actual field conditions. R. M. Smith *et al.*<sup>66</sup> deal with undisturbed soil samples by measuring the amount of water removed at various water tensions. In porosity measurements the distribution of pore sizes is often of greater concern than the total pore space. An arbitrary fractionation of ranges of pore size is based on the emptying of the different sized pores on the application of graduated water tensions. The "porosity factor" determined by these workers is the summation: percentage of pores drained at 10 cm. tension  $+ \frac{1}{4} \times$  (% of pores drained between 10 cm. and 40 cm. tension)  $+ \frac{1}{10} \times$  (% of pores drained between 40 cm. and 100 cm. tension). It is shown that the rate of percolation of water through soil is related to the diameter of water-filled pores and not to (diameter)<sup>2</sup> as would be required for the flow of viscous liquids. It is claimed that the physical condition of soil which controls movement of water is adequately defined only if percolation rates and the "porosity factor" are known. An example of methods of examination of disturbed soil samples is that described by P. S. Sreenivasan.<sup>67</sup> The principle involved is the relationship between rates of percolation through soil columns and the degree of compaction of the column. Various methods are available for measuring the compaction of undisturbed field samples. In the laboratory technique the "percentage

<sup>65</sup> *S. African J. Sci.*, 1945, **41**, 106; B., 1945, III, 201.

<sup>66</sup> R. M. Smith, D. R. Browning, and G. G. Pohlman, *Soil Sci.*, 1944, **57**, 197; B., 1944, III, 189.

<sup>67</sup> *Current Sci.*, 1942, **11**, 287; B., 1943, III, 29.



packing" ( $P$ ) is calculated as the decrease in volume of a loosely-filled cylinder of soil when a known pressure is applied and is expressed as a percentage of the maximum decrease resulting from the greatest pressure available. Percolation rates are measured by the length of the column (horizontally placed) through which water penetrates in a specified time. The author establishes a linear relationship between  $P$  and the percolation rate, and shows that curves for different penetration times converge on a common point, the "impervious point," at which percolation is zero. The packing pressure at the "impervious point" is a characteristic of individual soils. H. R. Christensen<sup>68</sup> tackles the problem by comparing the permeability of unsaturated soil to water in field and disturbed samples and utilises the relationship between permeability and capillary potential for wetting and drying as a basis for characterising soil in this respect. M. Fireman,<sup>69</sup> in recording tests made on disturbed samples of alkali soils, offers further confirmation that data so obtained can be translated satisfactorily into terms applying to field conditions. J. E. Christiansen<sup>70</sup> draws attention to errors introduced into permeability measurements made with soil packed in cylinders by entrapped air. In extreme cases apparent permeability values may be increased as much as 30-fold by evacuation of entrapped air before water is allowed to pass through the column. This serious error may arise even when water enters a vertical column of soil from below.

Porosity and permeability data represent the first stage of investigations of infiltration and drainage of water. The actual water content and, especially, daily variations in water content are matters of more immediate concern in cropping. Electrical devices figure largely in methods for constructing a continuous record of soil-water contents.<sup>71</sup> It is found, for example,<sup>72</sup> that the electrical resistance of soils, measured by means of electrodes encased in plaster of Paris, affords a convenient method for daily recording of soil-water contents with sufficient accuracy for the effective control of irrigation practice. R. H. White-Stevens and W. C. Jacob<sup>73</sup> describe a somewhat similar technique using alabastone in place of plaster of Paris. A. U. Momin<sup>74</sup> uses grid electrodes in conjunction with an amplifier unit for this purpose. In an investigation of some electrical properties of Indian soils S. M. F. Rahman and F. Muhi<sup>75</sup> indicate further developments in measurements of this kind. Utilising medium broadcast frequencies they show that electrical conductivity of soils increases with the frequency and with the water content of the

<sup>68</sup> *Soil Sci.*, 1944, 57, 381; B., 1944, III, 189.

<sup>69</sup> *Ibid.*, 58, 337; C., 1945, 128.

<sup>70</sup> *Ibid.*, 355; B., 1945, III, 69.

<sup>71</sup> *Ann. Repts.*, 1942, 27, 369.

<sup>72</sup> N. E. Edlefsen, A. B. C. Anderson, and W. B. Marcum, *Soil Sci.*, 1942, 54, 275; B., 1943, III, 117.

<sup>73</sup> *Proc. Amer. Soc. Hort. Sci.*, 1940, 37, 262; B., 1943, III, 165.

<sup>74</sup> *Proc. Indian Acad. Sci.*, 1944, 19, A, 100; B., 1944, III, 173.

<sup>75</sup> *Indian J. Physics*, 1944, 18, 31; B., 1945, III, 1.



soil, whereas the dielectric constant varies inversely with the frequency used and directly with the soil-water content.

The heat-conductivity of soil is also a satisfactory measure of its water content, and C. N. Johnson,<sup>76</sup> using a heating element with a casing of plaster of Paris, which rapidly reaches water equilibrium with the soil, demonstrates that at two critical water contents, viz., field capacity and wilting point, the technique yields similar data in different types of soil in which the actual water contents may be widely different. An apparatus for determining soil-water content by the calcium carbide method is described by White-Stevens and Jacob.<sup>66</sup> Carbide and moist soil are placed in separate compartments of a special container and the whole is weighed. The contents of the two compartments are mixed and the loss in weight during the reaction is ascertained.

Further attention has been given to measurements of the suction force of soil-water, now generally expressed in  $pF$  units, and to the relation of these measurements to the availability of soil-water to crops. The construction of the complete  $pF$  curve is discussed by P. R. Day<sup>77</sup> and by A. L. C. Davidson and R. K. Schofield.<sup>78</sup> The last-named authors bridge the gap in the curve between the upper limit of measurement by the filter apparatus (400 cm. suction) and the lower limit of those by the freezing point method (4000 cm.) by the use of calibrated absorbers or tensiometers constructed from thin plates of Portland stone. L. A. Richards and L. R. Weaver<sup>79</sup> examine  $pF$  curves over a wide range of conditions in Californian soils, giving special attention to water contents in the neighbourhood of the wilting point. For sunflower plants this range is 5—13 atm. for initial wilting and 20—30 atm. for the ultimate wilting point. The data suggest that the movement of soil within the wilting range is not entirely accounted for by the diffusion of vapour. In a further discussion of  $pF$  curves H. A. Wadsworth<sup>80</sup> contends that the sigmoid form of soil-moisture-vapour pressure curves is due to the combined effects of two processes of water absorption: (i) a surface absorption largely associated with low vapour pressures and operating in accordance with the Williams-Henry law of unimolecular absorption, and (ii) condensation of water vapour in the interstices of soil in amounts which increase rapidly with rise in vapour pressure. According to this author the water content-vapour pressure curve is not necessarily a soil characteristic since it is influenced considerably by conditions (notably of wetting and drying) to which the sample has been subjected prior to examination.

Numerous records of the application of tensiometer measurements to field problems have appeared in recent years. Among these may be cited

<sup>76</sup> *Soil Sci.*, 1942, **54**, 123; B., 1944, III, 2.

<sup>77</sup> *Ibid.*, 391; B., 1943, III, 197.

<sup>78</sup> *J. Agric. Sci.*, 1942, **32**, 413; B., 1943, III, 29.

<sup>79</sup> *Soil Sci.*, 1943, **56**, 331; B., 1944, III, 82. *J. Agric. Res.*, 1944, **69**, 215; B., 1945, III, 33.

<sup>80</sup> *Soil Sci.*, 1944, **38**, 225; B., 1945, III, 53.



the investigations of Veihmeyer *et al.*,<sup>81</sup> who give data for the upper half of the range of moisture content between the wilting point and the moisture equivalent in soils cropped with sunflower, strawberries, and Sudan grass. Similarly E. M. Anderson<sup>82</sup> establishes the rate of depletion of soil-moisture brought about in a deep peat by the growth of lettuce and M. B. Russell *et al.*<sup>83</sup> record a somewhat more detailed investigation in connexion with the growth of maize. In the latter work maize was found to obtain its moisture at first from shallow soil layers immediately beneath the "hills" and then to extend the zone of absorption laterally to similar depths. Later the area of soil affected was increased laterally to progressively greater depths. The effects of cultivation practices, notably terracing, on the retention of water by soils are examined tensiometrically by Knoblauch *et al.*<sup>84</sup> A. C. Evans<sup>85</sup> also uses this method in a survey of wireworm distribution in relation to soil-water content.

### *The Wilting Point.*

Although in recent years some doubt has been cast on the value of the wilting point as a soil characteristic, the practical significance of wilting ensures the maintenance of considerable interest in the possible correlation of wilting points with other "single-value" constants of soils. J. R. Furr and J. O. Reeve<sup>86</sup> in a recent paper show that over the range of soil-moisture contents from the field capacity to the first permanent wilting point there is a progressive increase in the osmotic pressure of the plant sap amounting to about 5 atm. in dry and 2.5 atm. in moist air. These changes correspond to a diffusion-pressure deficit of about 9 atm. at the first and 22 atm. at the ultimate permanent wilting point. The water held by the soil between the first and ultimate wilting points averages (among different soil types) 20% of that held between the ultimate wilting point and the moisture equivalent. The soil-water contents at the first and ultimate wilting points serve as points of reference for differentiating between water available merely to maintain the life of the plant and that which is utilisable for vegetative growth. Such observations are of value in the operation of irrigation systems. R. F. Williams and T. J. Marshall,<sup>87</sup> working with sunflowers in Australian soils, also establish a relationship between the mechanical equivalent and the permanent wilting point moisture, which is substantially constant in soils of the same type but shows considerable variation among soils of different types. The lack of constancy of the wilting point as a soil characteristic has been explained

<sup>81</sup> F. J. Veihmeyer, N. E. Edlefsen, and A. H. Hendrickson, *Plant Physiol.*, 1943, 18, 66; B., 1944, III, 106.

<sup>82</sup> *Proc. Amer. Soc. Hort. Sci.*, 1940, 37, 693; B., 1943, III, 201.

<sup>83</sup> M. B. Russell, F. E. Davis, and R. A. Bair, *J. Amer. Soc. Agron.*, 1940, 32, 922; B., 1944, III, 222.

<sup>84</sup> H. C. Knoblauch, H. C. Lint, and S. J. Richards, *Proc. Soil Sci. Soc. Amer.*, 1942, 6, 480; B., 1943, III, 2.

<sup>85</sup> *Nature*, 1943, 152, 21; B., 1943, III, 229.

<sup>86</sup> *J. Agric. Res.*, 1945, 71, 149; B., 1945, III, 239.

<sup>87</sup> *J. Austral. Inst. Agric. Sci.*, 1942, 8, 109; B., 1943, III, 29.



on the basis of its dependence on the character and, perhaps, the physiological condition of the plant and also on environmental conditions, notably temperature and atmospheric humidity. R. F. Daubenmire and H. E. Charter<sup>88</sup> record some data bearing on these points. In the soils examined the wilting of a number of woody desert legumes occurs at the same level of water content as does that of wheat. In the legumes growth and transpiration rates are substantially constant at all soil-moisture contents above the wilting point. At the wilting point, growth ceases and transpiration is markedly reduced. It would appear that transpiration rates are closely related to the intensity of illumination rather than to the evaporative power of the atmosphere as is often supposed. The work reported affords further evidence of the varied nature of the factors influencing the wilting of plants, clarification of which appears to be essential if the wilting point moisture of soils is to be utilised satisfactorily in field work.

An interesting paper by P. J. Kramer<sup>89</sup> indicates the possibility of employing another, and perhaps related, plant phenomenon as a criterion of the soil-water status in substitution for or as supplement to wilting. Removal of the tops of plants (*Coleus*, sunflower, and tomato are examined) just above the root crown is followed by exudation of sap from the cut stump. This exudation occurs only when the available water content of the soil exceeds a certain limiting value which, in the soil examined, was 45% of the water available to the intact plant. It is claimed that the soil-water content at which exudation is just prevented is as characteristic of the soil as is the wilting point or the moisture equivalent.

#### *Soil-Water and Plant Development.*

The effects of an insufficient water supply on crop growth, yield, and quality are, in a general sense, clearly recognised. The extent of recent research on the more specific physiological and biochemical effects of drought conditions is such as to justify the conclusions that the need of a more detailed understanding of water-plant relationships is a very real one and that the clarification of these relationships may have extensive practical as well as academic significance.

Investigations of the influence of the level of water supply on fundamental processes in plants are illustrated by that of N. F. Childers and G. W. Schneider,<sup>90</sup> who examine the effect of diminished soil-moisture supply in lowering the rate of photosynthesis in apple leaves under varying conditions. As the wilting point is approached the photosynthetic rate falls as much as 80% below its normal value. The transpiration rate falls to a similar extent and respiration is simultaneously increased. The relative inhibition of photosynthesis is more rapid at

<sup>88</sup> *Bot. Gaz.*, 1942, 103, 762; A., 1945, III, 69.

<sup>89</sup> *Amer. J. Bot.*, 1941, 28, 446; B., 1944, III, 252.

<sup>90</sup> *Proc. Amer. Soc. Hort. Sci.*, 1940, 37, 365; A., 1943, III, 700.



higher temperatures. D. F. Allmendinger *et al.*,<sup>91</sup> also working with apple trees, record no appreciable alteration in carbon dioxide uptake until the soil-water content falls to about 3% above the wilting point. In a somewhat similar study of the cotton plant V. A. Brilliant<sup>92</sup> examines the effect of exposure to dry conditions at intervals. The first exposure produces certain irreversible changes in the plant cells and sets up the condition of "drought hardening." Subsequent exposures, following intermediate periods under normal growth conditions, produce relatively smaller changes, *e.g.*, in depression of photosynthesis, associated with a diminution in water content of the plant of 20—23% of the fresh weight.

Disturbances in the nitrogen metabolism of plants due to deficiency of water are examined by A. H. K. Petrie *et al.*<sup>93</sup> Although the percentage intake of nitrogen by tobacco plants is increased by a restricted water regime, the rate of protein synthesis diminishes probable as a result of a limited carbohydrate supply, with the result that the maximum percentage of protein in the leaf is attained more slowly than in normally watered plants. H. T. Northen<sup>94</sup> indicates actual fission of protein in leaves to be a consequence of drought conditions, this change being accompanied by hydrolysis of polysaccharide reserves and increased respiration.

Relationships between the nutrient status of the soil and the effects of water supply on plants are considered in a number of publications. Thus V. A. Novikov<sup>95</sup> records that premature shedding of buds and bolls in cotton associated with dry soil conditions (or other conditions limiting photosynthesis) may be prevented by (among other practices) supplying adequate amounts of nitrogen, potash, and phosphate to the plants. According to F. M. Eaton<sup>96</sup> plants growing in dilute nutrients tend to produce a larger root system and to take up more water than when grown in a richer medium. The bearing of these observations on manurial and irrigation practices is an obvious one. It would appear, however, that the vital factor on which the utilisation of water by plants depends is the total concentration or osmotic pressure of the nutrient substrate rather than the relative proportions of individual nutrients present. Indirect confirmation of this observation is given by experiments of C. H. Wadleigh and A. D. Ayers,<sup>97</sup> who show that the addition of common salt to soil induces some, at least, of the symptoms of water deficiency in respect of diminished growth, disturbed nitrogenous metabolism, and lowered starch content.

<sup>91</sup> D. F. Allmendinger, A. L. Kenworthy, and E. L. Overholser, *Proc. Amer. Soc. Hort. Sci.*, 1943, 42, 133; A., 1945, III, 73.

<sup>92</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 219; A., 1945, III, 144.

<sup>93</sup> A. H. K. Petrie, J. I. Arthur, and J. G. Wood, *Austral. J. Exp. Biol.*, 1943, 21, 191; A., 1944, III, 377.

<sup>94</sup> *Bot. Gaz.*, 1942, 104, 480; A., 1944, III, 780.

<sup>95</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32, 148; B., 1943, III, 72.

<sup>96</sup> *Plant Physiol.*, 1941, 16, 545; A., 1945, III, 141.

<sup>97</sup> *Ibid.*, 1945, 20, 106; A., 1945, III, 586.



The influence of water supply on flowering and seed production is examined by F. D. Skazkin,<sup>98</sup> who shows that drought during the heading period of oats leads to a diminution in carbohydrate content and an increase in soluble nitrogen at the expense of protein, both conditions tending to restrict flowering and setting. M. W. Reger<sup>99</sup> also refers to delayed flowering in ornamental plants caused by low soil-water content. Similar effects in the case of flax are reported by F. L. Milthorpe<sup>100</sup> and in lucerne by C. O. Granfield.<sup>101</sup> N. S. Tiver and R. F. Williams<sup>102</sup> note the marked reduction of oil yield per acre from linseed following drought at and after the flowering stage and attribute this in part to the smaller set of flowers and in part to changes in the nitrogen status of the plants resulting from restricted assimilation. The actual percentage of oil in the seed is only slightly affected. A number of American workers<sup>103</sup> have investigated the ill-effects of water deficiency on the growth and quality of pears. Water shortage, even to a depth of 4 feet, adversely affects the growth rate of the fruit, and such fruit has an abnormally low sugar content per unit dry matter and a lower water content. The mature fruit has, however, greater sweetness and acidity, is firmer, and respire more slowly than that grown with a generous water supply. The ratio of soluble solids to total sugar in the juice remains unchanged and the storage quality of the fruit is unaffected.

A serious problem in irrigation practice, on which many of the above observations have a bearing, is that of ascertaining the most effective frequency of application of the water as well as the total amount to be given and the stages of growth at which the effects are the most profitable. W. W. S. Anderson<sup>104</sup> examines the influence of frequency of watering on the growth of sweet potatoes. Daily applications produced greater yields of better-quality tubers than did equivalent weekly watering. Shoot growth was much less affected than that of roots by the difference in watering practice. The influence of frequency of irrigation on the growth of "tanglehead" grass (*Heteropogon contortus*) investigated by G. E. Glendening<sup>105</sup> represents another aspect of a similar problem, complicated, in this instance, by the factor of competition. It is established that maximum growth (dry weight per plant) results from the most frequent watering and least competition, whereas maximum shoot/root ratio is associated with frequent watering and intense competition. Apparently tillering of the plants is largely influenced by the production

<sup>98</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 27, 1042; A., 1945, III, 332.

<sup>99</sup> *Proc. Amer. Soc. Hort. Sci.*, 1942, 39, 381; B., 1943, III, 144.

<sup>100</sup> *Ann. Bot.*, 1945, 9, 31; A., 1945, III, 265.

<sup>101</sup> *J. Agric. Res.*, 1945, 70, 123; B., 1945, III, 118.

<sup>102</sup> *Austral. J. Exp. Biol.*, 1943, 21, 201; A., 1944, III, 377.

<sup>103</sup> A. H. Hendrickson and F. J. Veihmeyer, *Proc. Amer. Soc. Hort. Sci.*, 1942, 39, 1; 1942, 40, 13. F. W. Allen, *ibid.*, 1943, 41, 106. A. L. Ryall and W. W. Aldrich, *J. Agric. Res.*, 1944, 68, 121; B., 1943, III, 143, 171; A., 1944, III, 440.

<sup>104</sup> *Proc. Amer. Soc. Hort. Sci.*, 1942, 39, 290, 295; A., 1943, III, 534; B., 1943, III, 167.

<sup>105</sup> *Bot. Gaz.*, 1941, 102, 684; B., 1945, III, 2.



of adventitious roots, which, in turn, is dependent on adequate supplies of water in the surface layer of the soil. Of the two factors, surface water supply is of greater significance than competition in controlling the growth of the grass.

### *Soil Aëration.*

Although shortage of soil-moisture is the more general and more obvious cause of crop failure, an excessive water content, nevertheless, frequently brings in its train adverse effects on the growth of plants. In some cases the lowering of soil temperature or the dilution of nutrient minerals in very wet soils may contribute materially to unfavourable growth conditions, but in a great many instances the important factor concerned is the restricted aëration of the soil. Lack of oxygen may place severe restrictions on the development and activity of plant roots, may result in injurious accumulations of carbon dioxide in the soil atmosphere, and may favour the activity of harmful at the expense of beneficial soil micro-organisms with far-reaching and complex effects on the nutrient status. N. F. Childers *et al.*<sup>106</sup> record that excessive watering of young apple trees seriously lowers the rates of transpiration and photosynthesis and that actual flooding reduces both these activities to as little as 5% of normal. In sugar beet heavy prolonged rainfall is shown by I. Belikov<sup>107</sup> to cause a marked decline in sugar accumulation, the condition being prevented by practices facilitating soil drainage, *e.g.*, liberal use of organic manures, loosening of soil, under-drainage, sowing on ridges, etc.

Root growth is closely related to the oxygen content of the soil atmosphere, and this is investigated by D. Boynton<sup>108</sup> in the case of apple trees. Diminution in the oxygen content of the soil-air below 15% markedly decreases the production of new rootlets and below 10% the growth of the trees is seriously affected. These unfavourable conditions are accentuated if the decrease in oxygen content is accompanied, as is usually the case, by an increase in the proportion of carbon dioxide. Similar results have been obtained<sup>109</sup> with peach and prune trees grown in nutrient solutions. Here again 15% of oxygen in the aërating gas represents a critical value for root growth. Apple trees under the same conditions show a progressive increase in root growth with rise in oxygen concentration over the whole range of 5—20%. In a series of papers<sup>110</sup> F. Hardy and colleagues seek to correlate the growth of cacao trees with the aëration of a soil during the few months of the year when the soil is not waterlogged. During about 3 months the relative proportions of water and air filling the pore space of the soil are suitable for maximum growth.

<sup>106</sup> N. F. Childers, D. G. White, and F. W. Southwick, *Proc. Amer. Soc. Hort. Sci.*, 1941, 38, 163; A., 1943, III, 612.

<sup>107</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 351; B., 1945, III, 37.

<sup>108</sup> *Proc. Amer. Soc. Hort. Sci.*, 1940, 37, 19; B., 1943, III, 168.

<sup>109</sup> D. Boynton and O. C. Compton, *ibid.*, 1943, 42, 53; B., 1944, III, 249.

<sup>110</sup> H. Vine, V. A. Thompson, and F. Hardy, *Trop. Agric. [Trinidad]*, 1943, 20, 13, 51; F. Hardy, *ibid.*, 89; B., 1945, III, 85; C., 1945, 128.



It is shown that when the air space of the soil falls short of 12% of the total soil volume, diffusion of air is considerably restricted, carbon dioxide accumulates in the soil-air, and anaërobic conditions predominate. The authors introduce a novel means of assessing the degree of soil aëration by driving clean iron spikes in to soil to varying depths and noting the amount of corrosion occurring in 14 days. The method yields satisfactory field data in soils which are not excessively acid (pH not below 4.3) and have only a moderate salt content.

### ORCHARD SOILS.

Many of the problems of the management of orchard soils are concerned with the conservation of moisture, especially at periods when the vital processes of fruit development and ripening are taking place. A number, too, are nutritional problems; often the two are interrelated. In permanent grass orchards the feeding of the trees often resolves itself into surface applications of fertilisers or lime; the supply of moisture is dictated by local conditions and little is done to modify this state of affairs.

In many cases grassed orchard soils do not produce the best crops either in yield or quality unless special precautions are taken. The trees are subject to constant competition for water and nutrients by the grass and the permanent covering tends to limit the infiltration of rain to the sub-soil, this latter being the more notable factor since it is less easily counter-acted. Lack of soil aëration may also lead to unsatisfactory growth conditions especially in the heavier types of soil.

It is with such considerations in view that many investigations of orchard soils include studies of various practices, *e.g.*, cover-cropping, cultivation, and mulching, which may increase the nutrient supply in the soil or improve its water status—often a more important matter. W. P. Judkins and H. A. Rollins,<sup>111</sup> among a number of workers, compare the effects of permanent grass, cover cropping, and mulched grass on tree growth. Differences in soil-moisture content under the three conditions were not great but cover-cropping and mulched grass produced the better growth of peach trees. This is, at least in part, to be ascribed to differences in nitrate content of the soil during July—September being greatest in cover-cropped and least in the grassed soils. L. Y. Li,<sup>112</sup> working on New Zealand soils, obtained improved results with inter-cropping (two crops per annum) associated with greater infiltration of water into the soil. Mulching with plant material as compared with bare cultivation is shown by Burvill *et al.*<sup>113</sup> in Australia to increase the retention of water in orchard soils during summer, provided the growth of weeds was prevented. Growth of weeds or cover-cropping lowered the water retention of the soil, especially if spring ploughing was delayed. This

<sup>111</sup> *Proc. Amer. Soc. Hort. Sci.*, 1943, **43**, 7; B., 1944, III, 249.

<sup>112</sup> *New Zealand J. Sci. Tech.*, 1943, **25**, A, 86; B., 1944, III, 121.

<sup>113</sup> G. H. Burvill, L. J. H. Teakle, and L. T. Jones, *J. Dept. Agric. W. Australia*, 1943, **20**, 224; B., 1945, III, 217.



observation concerning cover crops is perhaps related to a conclusion reached by A. F. Pilsbury and M. R. Huberty<sup>114</sup> that the infiltration of water into soil is not accelerated by cover-cropping until after the crop is cut and the residues are partially decayed. J. K. Shaw<sup>115</sup> records experiments in which the mulching of apple orchard soils with poor hay produces better yields of apples than those from cover-cropped or bare cultivated soils. This is associated with better infiltration, better aëration, and higher nitrate content of the soil, and a tendency to encourage the growth of surface-feeding roots in the mulched soil. As compared with clean cultivation heavy mulching with straw is reported by I. W. Wander and J. H. Gourley<sup>116</sup> to result in increased supplies of available calcium, magnesium, phosphate, borate, and, especially, potassium in the soil. The effect on the potassium content was apparent to a depth of 2 feet whereas that on boron and phosphate was limited to the surface layer immediately under the mulch. C. E. Baker<sup>117</sup> also comments on the increased potassium content of apple leaves following mulching with inorganic materials (cinders, glass wool), an effect ascribed to increased availability of soil-potassium or to the production of rootlets feeding near the surface where the available potassium content is normally maximum. Beneficial effects of mulching and of cover-cropping in peach orchards are demonstrated by J. B. Rogers,<sup>118</sup> A. D. Hubbard,<sup>119</sup> and J. T. Bregger and A. M. Musser,<sup>120</sup> from whose joint observations there emerges evidence in favour of the practice of growing an autumn-sown cover crop, restricting the competition of the crop for moisture and nutrients by frequent summer cultivation, or by mowing the crop and leaving it on the surface as a mulch. It would appear that supplementary dressings of nitrogenous fertilisers to the cover crops are necessary to ensure its rapid growth and to maintain a suitable level of nitrogen supply for the fruit. A communication from Pennsylvania<sup>121</sup> adds confirmation of the satisfactory nature of this practice in peach orchards; in apple orchards the use of supplementary nitrogen fertilisers may be omitted if a leguminous cover-crop is used. A further advantage of mulching noted by R. J. Barnett<sup>122</sup> is that of restricting the penetration of frost into orchard soils. Some adverse effects of cultivation on orchard soils described by R. E. Stephenson and C. E. Schuster<sup>123</sup> include loss of organic matter, diminution in the availability of phosphate, and the impoverishment of soil structure including the formation of plough-pans.

<sup>114</sup> *Proc. Amer. Soc. Hort. Sci.*, 1942, 39, 16; B., 1943, III, 141.

<sup>115</sup> *Ibid.*, 1943, 42, 30; B., 1944, III, 246.

<sup>116</sup> *Ibid.*, 1; B., 1944, III, 246.

<sup>117</sup> *Ibid.*, 7; B., 1944, III, 246.

<sup>118</sup> *Ibid.*, 43, 17; B., 1944, III, 241.

<sup>119</sup> *Ibid.*, 1944, 44, 66; B., 1945, III, 6.

<sup>120</sup> *Ibid.*, 1940, 37, 1; B., 1943, III, 204.

<sup>121</sup> Anon., *Pennsylvania Agric. Exp. Sta.*, 1942, *Bull.* 431; B., 1945, III, 89.

<sup>122</sup> *Proc. Amer. Soc. Hort. Sci.*, 1944, 44, 57; B., 1945, III, 36.

<sup>123</sup> *Soil Sci.*, 1942, 54, 325; B., 1943, III, 197.



## LIGHT AND PLANT GROWTH.

As an essential factor in plant development, light has received more consideration from the academic than from the practical viewpoint. That sunlight is vitally concerned in the growth of plants is not only common knowledge but is also a matter of common observation to those whose agricultural or horticultural activities are of the very slightest. In general, sunshine implies growth, and the emphasis is popularly placed on the intensity of light rather than on its duration as a measure of its action. We are accustomed to climatic conditions in which long days, bright sunshine, higher temperatures, and kindlier soil conditions operate simultaneously and beneficially on the growing plant, and the true significance of the light factor is apt to be obscured. The plant physiologist recognises that in addition to the intensity of light to which a plant is exposed its duration, the "day-length" or photoperiod, is also a matter of importance. It is clear that the photosynthetic process contributes a very large proportion of the plant's substance and that this process is dependent on the absorption and utilisation of solar energy by the plant. It does not follow, however, that the growth of the plant is proportional to the gross amount of light energy radiated even when nutritional and environmental conditions are optimum. That the quality of the light received, *i.e.*, the wave-length distribution, is also concerned is demonstrated by many workers, among whom may be cited R. E. Cooper and R. R. Ullal,<sup>124</sup> L. M. Rohrbaugh,<sup>125</sup> F. W. Went,<sup>126</sup> and R. B. Withrow.<sup>127</sup>

From numerous investigations in recent years it has become evident also that the rhythmic light-dark cycle of the photosynthetic process may be influenced in its effects by the relative lengths of the light and dark periods. It is further established that different plant species do not respond in the same manner to changes in this periodicity. In fact, plants may now be classified as "long-day" or "short-day" plants according to their response to the duration of the photoperiod. The period of exposure to light, therefore, emerges as a factor having an individual as well as a contributory function in the sense that the total energy absorbed, itself a primary factor in photosynthesis, is a function of both light intensity and its duration. Any attempt to disentangle this dual function of the photoperiod would be not only premature but also beyond the scope of this Report. The present concern is the consideration of some recent research having a bearing on certain practical aspects of the influence of the length of the photoperiod on plant growth. This relates largely to horticultural subjects, *e.g.*, decorative and flowering plants, for which supplementary lighting or shading is a practical possibility. The application of the results of recent work to field crops is a more speculative subject in so far as it affords explanation of some effects of weather

<sup>124</sup> *J. Indian Bot. Soc.*, 1940, **18**, 139; A., 1944, III, 230.

<sup>125</sup> *Bot. Gaz.*, 1942, **104**, 133; A., 1944, III, 780.

<sup>126</sup> *Amer. J. Bot.*, 1941, **28**, 83; A., 1944, III, 854.

<sup>127</sup> *Plant Physiol.*, 1941, **16**, 241; A., 1944, III, 313.



conditions on crop growth and, as our knowledge of the subject expands, may contribute to the accuracy of forecasts of crop yield or quality, or even in some cases indicate possible treatment of the growing crop (manuring, disbudding, defoliation, etc.) to offset adverse effects of particular seasonal conditions. The recognition of "long-day" and "short-day" types of plants may well serve as a guide in the introduction of commercial crops into new areas.

As an illustration of the operation of the light factor in field cropping may be cited the work of T. E. Aurén,<sup>128</sup> who shows that the utilisation of solar energy in sugar production by sugar beet is more efficient in the later than in the earlier stages of growth when the day-length is shorter. Moreover, sugar production is directly related to the amount of solar energy received up to a critical level corresponding to 80—85 g. of sugar per root, the influence of further energy being variable presumably as a result of the operation of other metabolic factors. In an examination of cotton by F. M. Eaton and N. E. Rigley<sup>129</sup> premature boll-shedding is associated with diminished carbohydrate supply in the plants and therefore with the intake of solar energy. In view of the general relationship between the carbohydrate and nitrogen metabolism in plants the observation has a probable bearing on the nitrogen nutrition of cotton. H. M. Beachell<sup>130</sup> records that rice subjected experimentally to a 10-hour photoperiod headed earlier than that grown under normal conditions. On the other hand, interruption of the normal photoperiod by covering the plants for part of the day caused later than normal heading. Differences in growth habit are shown by I. H. Stuckey<sup>131</sup> to occur in grass seedlings due to changes in photoperiod, a 16-hour day producing longer leaves and more erect growth than does an 8-hour day. Relationships between the length of the photoperiod and the nitrogen nutrition of tobacco are examined by R. A. Dennison,<sup>132</sup> a short period (6.5 hours) being associated with slower stem growth, smaller but more numerous leaves, less flowering, and smaller total yield than is a long period (16 hours). The response of plants to manurial treatment generally is affected by the suitability or otherwise of the photoperiod. M. C. Tschajlatschjan and E. K. Lukovnikov<sup>133</sup> record this in typical short-day (oats) and long-day (millet) plants. The reverse phenomenon, viz., the inability of plants to respond to favourable day-length unless the mineral nutrient supply is adequate, is also shown by these authors. An example of the effect of the photoperiod on the form of growth of plants is given by L. L. Danielson<sup>134</sup> in the case of cucumber. Leaf size reaches maximum with a 12-hour day and total dry matter production with a 12—16-hour

<sup>128</sup> *Arkiv Bot.*, 1943, 30, A, No. 15; A., 1944, III, 705.

<sup>129</sup> *Plant Physiol.*, 1945, 20, 380; A., 1945, III, 900.

<sup>130</sup> *J. Agric. Res.*, 1943, 66, 325; A., 1944, III, 705.

<sup>131</sup> *Amer. J. Bot.*, 1942, 29, 92; A., 1945, III, 92.

<sup>132</sup> *Plant Physiol.*, 1945, 20, 183; A., 1945, III, 702.

<sup>133</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32, 152; A., 1943, III, 444.

<sup>134</sup> *Plant Physiol.*, 1944, 19, 638; A., 1945, III, 647.



day, whereas staminate flower production is greatest with an 8-hour day.

In this field of research much attention has been given to flowering and decorative plants. According to L. K. Mann<sup>135</sup> the initiation of flowering organs in *Xanthium* and the rate at which they develop may be accelerated, according to the day-length to which they are exposed, up to a maximum beyond which lengthening of the photoperiod brought no further response. The influence of the photoperiod is further increased by increasing the intensity of the light; moreover the minimum period of exposure necessary to induce flowering is diminished by rising temperature. This investigation is typical of many and serves to illustrate the interdependence of environmental factors on flower formation. The process of flowering is commonly preceded by the accumulation of carbohydrate in certain classes of plants. If therefore a "long-day" plant such as *Hyoscyamus niger*, examined by G. Melchers and A. Lang,<sup>136</sup> is grown under "short-day" conditions delayed flowering results. In this case artificial infiltration of sugars into the plant provides the necessary stimulus to hasten the initiation of flower buds. Similar results are recorded in another publication<sup>137</sup> by conserving carbohydrates in plants by placing them in an oxygen-free atmosphere, thereby restricting respiration. Peanut, by contrast, flowers more readily under short-day conditions and investigations of A. I. Tscheliadinova<sup>138</sup> and of T. A. Lebedeva<sup>139</sup> show that the yield of seed and the fat content are lowered by long-day conditions. Shading the plants results in increased chlorophyll contents in the leaves. In this case the influence of "short-day" treatment for a period before flowering accelerates the process; the transfer of normal plants to short-day conditions at the beginning of the flowering period suffices to increase the seed yield. The practical implication here seems to be that a shaded position and close planting are likely to favour large yields.

The flowering of chrysanthemum, another "short-day" plant, may be controlled over a considerable period by modification of the lighting regime. E. P. Hume<sup>140</sup> records that cuttings grown under "long-day" conditions may be induced to form flower buds by 20 days' exposure to "short-day" conditions. The number of blossoms may be increased, according to M. C. Tschajlatschjan,<sup>141</sup> by placing the plants in darkness for five days and subsequently exposing them to short (9-hour) photoperiods and supplementing the supply of nitrogen to the roots. Infiltration of sugars delays flowering in contrast with the case of "long-day" plants. In practice it is often advisable to retard flowering and, as is to be anticipated, this may be achieved by exposure to long photoperiods. The

<sup>135</sup> *Bot. Gaz.*, 1940, **102**, 339; A., 1944, III, 84.

<sup>136</sup> *Naturwiss.*, 1942, **30**, 589; A., 1943, III, 361.

<sup>137</sup> G. Melchers and H. Claes, *ibid.*, 1943, **31**, 249; A., 1944, III, 230.

<sup>138</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 276; A., 1944, III, 84.

<sup>139</sup> *Ibid.*, 1940, **27**, 264; A., 1945, III, 900.

<sup>140</sup> *Proc. Amer. Soc. Hort. Sci.*, 1941, **38**, 665; A., 1943, III, 537.

<sup>141</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **44**, 348; A., 1945, III, 264.



flowers produced are generally of larger size.<sup>142</sup> A similar but more prolonged effect is produced by N. W. Stuart<sup>143</sup> by interrupting the dark period at about midnight by a short light exposure (about 30 minutes). Such treatment, if commenced about 10 days before visible bud formation, delays flowering for 2—3 months. With plants responding to "long-day" treatment, *i.e.*, supplementary lighting, the intensity of the additional light may affect the results obtained. Thus with *Aster chinensis* var. Heart of France, R. Wenger<sup>144</sup> produced maximum acceleration of flowering and number of flowers per plant by supplementary lighting of low intensity (0.3 foot-candle). When light of high intensity (100 foot-candles) was used vegetative growth was stimulated. Here again the difference in effects appears to hinge on the use to which carbohydrates and soluble nitrogen compounds are put by the plant. According to E. S. M. Sakr<sup>145</sup> the, usually unwanted, production of flowering stems in turnips is favoured by a long (16-hour) photoperiod, provided temperature conditions are appropriate, an essential preliminary being a low-temperature period (4—10°). Data concerning the photoperiodic response of a number of florists' crops are given by K. Post<sup>146</sup> and of various vegetable crops by F. L. Milthorpe and B. Horowitz.<sup>147</sup> H. A. Allard and W. W. Garner<sup>148</sup> in a general consideration of the effects of length of day on numerous native and cultivated plants point out that although a general classification of species into "long-" and "short-day" plants is possible, the range of sensitivity of individual members of these groups is often very divergent.

#### GROWTH-PROMOTING SUBSTANCES.

The tendency to refer to these substances as "plant hormones" is deprecated by many authorities. It is argued that the term "hormone" was introduced to describe the group of physiologically active materials secreted by the endocrine glands in animals. The "growth-promoting substances" occurring naturally in the plant world appear to be metabolic products rather than specific secretions and the existence in plants of organs corresponding to endocrine glands in animals has yet to be proved. The animal kingdom certainly has the advantage of prior usage. Pending further considerations of this point the term "growth-promoting substance" or "growth-substance," in spite of its lack of specificity of meaning, will be adopted in these Reports.

The horticultural applications of growth-substances were dealt with in these Reports<sup>149</sup> some years ago. The output of research work on this subject since that time has reached such dimensions as to demand its

<sup>142</sup> K. Post, *Proc. Amer. Soc. Hort. Sci.*, 1943, 43, 311; A., 1945, III, 68.

<sup>143</sup> *Ibid.*, 42, 605; A., 1944, III, 852.

<sup>144</sup> *Plant Physiol.*, 1941, 16, 621; A., 1945, III, 143.

<sup>145</sup> *Proc. Amer. Soc. Hort. Sci.*, 1944, 44, 473; A., 1945, III, 168.

<sup>146</sup> *Cornell Univ. Agric. Exp. Sta.*, 1942, *Bull.* 787; A., 1944, III, 230.

<sup>147</sup> *Agric. Gaz. New South Wales*, 1943, 54, 53; B., 1944, III, 84.

<sup>148</sup> *U.S. Dept. Agric.*, 1940, *Tech. Bull.* 727; A., 1943, III, 292.

<sup>149</sup> *Ann. Repts.*, 1941 26 376.



further consideration here. Many publications represent further elaboration or extended developments of matters to which reference was made previously. In this category fall two subjects of widespread practical interest, viz., the use of growth-substances in the vegetative propagation of plants and also in controlling flower and fruit production.

The rooting of hardwood cuttings still occupies much attention. Among various growth-substances examined for this purpose, B. G. Griffiths<sup>150</sup> finds indolylbutyric acid to give best results with Douglas fir and Sitka spruce, 80—100% rooted cuttings being obtained by placing the bases of the cuttings in a solution of the acid (25—50 p.p.m.) for 24 hours prior to planting. A later report by W. F. McCulloch<sup>151</sup> indicates that saplings obtained by this treatment tend to retain a branching habit and occasionally do not form a definite "leader" shoot. Black locust cuttings root readily after treatment with indolyl- or naphthyl-acetic acid (100 p.p.m.) for 24 hours, the effect being enhanced by storing treated cuttings at 21° before planting.<sup>152</sup> Differences in the optimum concentration of growth-substance used and in the period of treatment for different species are investigated by A. G. Snow<sup>153</sup> using softwood cuttings of maples. Solutions containing 50 p.p.m. of indolylbutyric acid gave best results with sugar maple and 200 p.p.m. with red maple. In general, 3-hour treatments are more effective than those of 24 hours for these species. According to F. L. O'Rourke<sup>154</sup> softwood cuttings of some, but not all, species of blueberry (*Vaccinium*) root more readily after dusting with indolylbutyric acid in talc (1 mg. per g.). Leaf bud cuttings of tropical shrubs examined by J. V. Watkins<sup>155</sup> and by H. H. Williams<sup>156</sup> respond to such dust treatments by production of heavier root systems, having longer and more branched rootlets and better shoot growth, than when solutions of the growth-substances were employed. In other cases, e.g., *Cinchona* and *Theobroma*, cuttings of which are normally difficult to root and show little response to commonly used concentrations (up to 100 p.p.m.) of growth-substance, positive results were obtained with more concentrated (500 p.p.m.) solutions.<sup>157</sup> Cuttings of *Forsythia suspensa*, which normally produce rootlets at the nodes, reacted to growth-substances by forming roots along the internodes without affecting the number of nodal roots.<sup>158</sup> It is evident that different species display considerable individuality in their response to growth-substances, a fact further emphasised by failure of workers to obtain any positive results,

<sup>150</sup> *J. Forestry*, 1940, **38**, 496; A., 1944, III, 156.

<sup>151</sup> *Ibid.*, 1943, **41**, 211; B., 1944, III, 147.

<sup>152</sup> V. T. Stoutemeyer, J. R. Rester, and F. L. O'Rourke, *ibid.*, 1940, **38**, 588; A., 1944, III, 156.

<sup>153</sup> *Ibid.*, 1941, **39**, 395; A., 1944, III, 155.

<sup>154</sup> *Proc. Amer. Soc. Hort. Sci.*, 1943, **42**, 369; B., 1945, III, 8.

<sup>155</sup> *Ibid.*, 1940, **37**, 1109; A., 1943, III, 698.

<sup>156</sup> *Ibid.*, 1943, **43**, 323; A., 1945, III, 77.

<sup>157</sup> W. C. Cooper, *ibid.*, 1944, **44**, 533; A., 1945, III, 27.

<sup>158</sup> *Ibid.*, 1943, **43**, 301; A., 1945, III, 67.



*e.g.*, with apple root-stocks, Norway spruce, grape vine, and by variable effects recorded with, *e.g.*, hops, juniper, and *Taxus*.

A. A. Prokofiev<sup>159</sup> describes some interesting results obtained in the treatment of cuttings of the rubber-bearing plant tau-saghyz. In general, the plant tends to produce a preponderance of either leaves or roots and only exceptionally the two organs simultaneously. Cuttings readily produce leaves but root formation is a relatively slow process. Treatment with a 0.1% solution of indolylacetic acid improved the growth of roots without appreciable change in leaf growth. With 0.2—0.5% solutions leaf formation was suppressed and rooting benefited accordingly. Further instances of the use of growth-substances to modify root/shoot ratios in plants include: that recorded by A. C. Gossard<sup>160</sup> in which injection of indolylbutyric acid into holes bored in the stems of young pecan trees induced accelerated root growth without affecting that of shoots; that of M. Levine and J. Lein<sup>161</sup> in which treatment of young onions with 10<sup>-8</sup>% indolylacetic acid improved root growth, and that of E. T. McEvoy<sup>162</sup> in which top growth and total dry weight of tobacco were increased by direct application of this growth-substance to the soil.

R. Castan<sup>163</sup> describes a more unusual effect of moderate concentrations of heteroauxin on plants, viz., the reversal of the general inhibition of axillary bud development associated with the growth of apical buds. High concentrations of the growth-substance will inhibit the growth of axillary buds already developing.

An association between the action of growth-substance and potash nutrition is reported by H. M. Laude<sup>164</sup> in the case of kidney beans. The plants grew more quickly (total dry weight) after addition of indolylacetic acid to the nutrient only when adequate supplies of potassium were present. The percentage of dry matter in the plant tissue increased with the level of potash nutrition, and increased succulence (lower percentage of dry matter) appeared only when high concentrations of the growth-substance were given. D. B. Swartz<sup>165</sup> also records that certain chrysanthemums which failed to respond to additions of indolylacetic acid to the nutrient did so in conditions of potash deficiency. It is not clear in such cases whether a direct action of potassium is concerned or whether the physiological effect of the growth-substance is linked with the carbohydrate metabolism of the plant which, in turn, is influenced by the supply of potassium.

The use of growth-substances to control flowering and the "setting" of seeds and fruits is the subject of much recent work. The varied results obtained suggest the need for much further investigation of the

<sup>159</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **42**, 233; A., 1945, III, 207.

<sup>160</sup> *Proc. Amer. Soc. Hort. Sci.*, 1942, **41**, 161; B., 1943, III, 173.

<sup>161</sup> *Amer. J. Bot.*, 1941, **28**, 163; A., 1944, III, 854.

<sup>162</sup> *Sci. Agric.*, 1942, **22**, 528; B., 1944, III, 223.

<sup>163</sup> *Compt. rend.*, 1943, **216**, 576; A., 1945, III, 335.

<sup>164</sup> *Bot. Gaz.*, 1941, **103**, 155; B., 1945, III, 4.

<sup>165</sup> *Ibid.*, 366; A., 1945, III, 77.



most appropriate conditions of application for specific purposes. According to P. C. Burrell and T. W. Whittaker<sup>166</sup> the setting of musk melons (normally poor, even if hand-pollinated) is much improved by treating the stigma, after pollination, with 1% indolylacetic acid in lanoline. A. E. Murneek *et al.*<sup>167</sup> show that repeated spraying of snap beans with naphthylacetic acid or its amide (5 p.p.m.), increased the yield of pods in hot seasons but has the opposite effect in a cool year. Similar use of a naphthylacetic acid dust (70—140 p.p.m.), on the other hand, is found by E. V. Hardenburg<sup>168</sup> to produce no beneficial effect and in some instances actually to decrease the yield. The fruit yield of strawberries is increased by spraying with naphthoxyacetic acid (20 p.p.m.), the increase being due to the greater size of individual fruits rather than to the larger number of fruits obtained.<sup>169</sup> More consistently beneficial effects on fruit setting are found with tomatoes by spraying at intervals during the flowering period with growth-substances. R. H. Roberts and B. E. Struckmeyer<sup>170</sup> gain best results with naphthoxyacetic acid (75 mg. per l.) but report that the same treatment of other subjects, *e.g.*, beans, peppers, strawberries, proves unsuccessful.  $\beta$ -Naphthoxy- and chlorophenoxyacetic acids are stated<sup>171</sup> to be superior to naphthylacetamide for this purpose. A secondary effect of the growth-substance is the stimulation of the outer regions of the pericarp of the tomato with consequent modification of the shape of the fruit, which, however, is unchanged in flavour or ascorbic acid content.

The production of parthenocarpic fruit by injecting growth-substances into the young ovaries, by spraying the flowers, or by the application of lanoline pastes has evoked much interest. During the process of seed production in fruits changes in the composition of the whole fruit or in the distribution of constituents in the various parts of the fruit may be considerable. As a consequence fruit formed without seeds or with fewer, or undeveloped, or infertile seeds may differ appreciably in composition from normal fruit. B. E. Janes<sup>172</sup> demonstrates this in the case of tomatoes and F. S. Howlett<sup>173</sup> notes also the absence of blossom-end rot in such fruit. A method of applying growth-substances, for greenhouse work, in the form of aerosols is described by P. W. Zimmerman and A. E. Hitchcock.<sup>174</sup> For this purpose a phenoxy-acid, *e.g.*, ethyl 4-chlorophenoxypropionate, is probably one of the most effective growth-substances in

<sup>166</sup> *Proc. Amer. Soc. Hort. Sci.*, 1940, **37**, 829; B., 1943, III, 235.

<sup>167</sup> A. E. Murneek, S. H. Wittwer, and D. D. Hemphill, *ibid.*, 1944, **44**, 428; B., 1945, III, 4.

<sup>168</sup> *Ibid.*, **45**, 367; B., 1945, III, 158.

<sup>169</sup> T. Swarbrick, *Ann. Rept. Agric. Hort. Res. Sta, Long Ashton*, 1943, 31; B., 1944, III, 223.

<sup>170</sup> *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 417; B., 1945, III, 88.

<sup>171</sup> A. E. Murneek, S. H. Wittwer, and D. D. Hemphill, *ibid.*, **45**, 371; B., 1945, III, 371.

<sup>172</sup> *Amer. J. Bot.*, 1941, **28**, 639; A., 1944, III, 783.

<sup>173</sup> *Proc. Amer. Soc. Hort. Sci.*, 1942, **41**, 277; B., 1943, III, 172.

<sup>174</sup> *Contr. Boyce Thompson Inst.*, 1944, **13**, 35; B., 1945, III, 35.



inducing fruit set and parthenocarpy in tomatoes. Blackberry flowers treated in this way by P. C. Marth and E. M. Meader<sup>175</sup> produce a heavier yield of fruit which still contains seeds but many of these are small and undeveloped. According to H. E. Clark and K. R. Kerns,<sup>176</sup> pineapple yields are increased by spraying with naphthylacetic acid, but high concentrations of the acid (0.05%) delay ripening and restrict the formation of slips and suckers.

Numerous investigations concern the effects of growth-substances on the flowering and fruiting of apples. Although these substances usually fail to stimulate the development of flower buds or to increase flower setting,<sup>177</sup> naphthylacetic acid and its amide in moderate concentrations may have a practical value in avoiding thinning by restricting the number of fruits formed.<sup>178</sup> Results of great commercial value are, however, obtained in preventing the premature fall of apples by spraying or dusting the trees during fruit growth with naphthylacetic acid.<sup>179</sup> A secondary advantage of such treatment is that fruit may be allowed safely to remain on the trees later before gathering with consequent improvement in the colour, size, and flavour of the more mature fruit.<sup>180</sup> Similar results are recorded for pears<sup>181</sup> and pecan nuts.<sup>182</sup>

The treatment of seeds with growth-substances has, in general, failed to improve germination or, in most cases, the subsequent growth of seedlings. Positive results are, however, recorded with tobacco seedlings by E. T. McEvoy,<sup>182</sup> with certain decorative plants by L. C. Chadwick and J. S. Swartley,<sup>183</sup> and with conifers by H. A. Fowells.<sup>184</sup>

Further horticultural uses of growth-substances are suggested by exploiting their inhibitory effect on shoot growth, which in many cases, notably in potato, represents a prolongation of dormancy. According to F. E. Denny,<sup>185</sup> satisfactory delay in potato sprouting is attained by treatment with methyl naphthylacetate (100 mg. per kg. of tubers) at temperatures not exceeding 12.5°. The quality of the potatoes for processing, *e.g.*, for chips, is unimpaired. The work of T. Swarbrick<sup>186</sup> suggests the possibility (often an economic advantage) of planting treated potatoes earlier than usual, delayed sprouting serving to avoid late frost

<sup>175</sup> *Proc. Amer. Soc. Hort. Sci.*, 1944, 45, 293; B., 1945, III, 160.

<sup>176</sup> *Bot. Gaz.*, 1943, 104, 639; A., 1944, III, 707.

<sup>177</sup> J. R. Magness, L. P. Batjer, and W. C. Baynes, *Proc. Amer. Soc. Hort. Sci.*, 1943, 43, 53; B., 1945, III, 4. Also L. Greene, *ibid.*, 42, 149; B., 1944, III, 247.

<sup>178</sup> G. W. Schneider and J. V. Enzie, *ibid.*, 167; 1944, 45, 63; B., 1944, III, 247; 1945, III, 159.

<sup>179</sup> M. B. Hoffman, A. V. Doren, and L. J. Edgerton, *ibid.*, 203; B., 1944, III, 247. Also L. Southwick, *ibid.*, 199; B., 1944, III, 247. Also C. W. Ellenwood and F. S. Howlett, *ibid.*, 193; B., 1944, III, 247.

<sup>180</sup> M. H. Haller, *ibid.*, 207; B., 1944, III, 247. Also E. P. Christopher and S. A. Pieniazek, *ibid.*, 43, 51; B., 1944, III, 248.

<sup>181</sup> A. E. Davey and C. O. Hesse, *ibid.*, 1942, 40, 49; B., 1943, III, 171.

<sup>182</sup> C. L. Smith, *ibid.*, 1944, 44, 119; B., 1945, III, 8.

<sup>183</sup> *Ibid.*, 1941, 38, 690; B., 1943, III, 174.

<sup>184</sup> *J. Forestry*, 1943, 41, 685; B., 1944, III, 146.

<sup>185</sup> *Contr. Boyce Thompson Inst.*, 1945, 14, 15; B., 1945, III, 241.

<sup>186</sup> *Ann. Rept. Agric. Hort. Res. Sta. Long Ashton*, 1943, 25; A., 1944, III, 782.



damage. Treatment of dormant rose trees with methyl or ethyl naphthylacetate or naphthylacetoneitrile in vapour form or as wax emulsions may prolong the dormancy for 40—60 days during storage or transport. According to P. C. Marth<sup>187</sup> treated trees are protected against mould growth and when planted out produce improved growth of both roots and tops.

The presence of auxin in soils has been demonstrated frequently, and a simple method of obtaining extracts suitable for the *Avena* test consists of shaking the soil with aqueous calcium hydroxide at pH 7—8 and subsequently concentrating the clear liquid.<sup>188</sup> J. H. Hamence<sup>189</sup> finds that a number of commonly used organic manures contain small amounts of growth-substance (usually, though not always, indolylacetic acid). Another source of growth-substance in soils is found by N. A. Krasilnikov<sup>190</sup> to be among the products of bacterial activity, notably of *Pseudomonas* species and *Azotobacter*.

<sup>187</sup> *Bot. Gaz.*, 1942, **104**, 26; A., 1944, III, 782.

<sup>188</sup> W. S. Stewart and M. S. Anderson, *ibid.*, **103**, 570; B., 1945, III, 1.

<sup>189</sup> *J.S.C.I.*, 1945, **64**, 147; B., 1945, III, 157.

<sup>190</sup> *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **45**, 80; A., 1945, III, 703.



# SUGARS.

BY NOEL DEERR, F.R.I.C.

THOUGH there have been no outstanding developments to record during the past twelve months a fair volume of new matter is available for review. This is particularly the case as regards India and the British West Indies, whence has derived most of the material included in this review. From another source attention has been directed to the use of sugar as raw material, one of the first publications of the newly founded Sugar Research Foundation, Inc., reviewing *in extenso* what has already been done in this connexion.

Last year attention was directed to the publication by the U.S. Bureau of Standards of an 800-page circular dealing with polarimetry. This has been supplemented by an equally extensive publication, "Bibliography of Solid Adsorbents," containing a detailed history of the use of carbons in sugar refining.

## CANE SUGAR MANUFACTURE.

R. D. E. Yearwood<sup>1</sup> has investigated the effect of trisodium phosphate on the removal of lime salts from cane juices. It was found that more lime was precipitated than corresponded with the quantity of sodium salt introduced, an effect traced to the precipitation of lime salts due to heating alone, and that when allowance was made for this the nett efficiency of the added phosphate was found to be only about 30%. It was stated by G. S. Warren that sugar boilers found that low-grade materials derived from juices which had been delimed were difficult to boil.

W. L. McCleery<sup>2</sup> advises liming to pH 8.3 followed by heating to 100°, provided that the increased volume of settlings can be handled, failing which it may be necessary to operate at a lower pH. J. G. Davies<sup>3</sup> remarks that in clarification with lime two objects have to be considered, the removal of non-sugars and the rate of settling; no procedure has yet been found that included the optimum of both these factors and it was necessary to operate at a compromised condition.

R. D. E. Yearwood<sup>4</sup> discusses the problem of the apparent loss of weight that occurs when cane is milled. While it has been found that this loss of weight is connected with the humidity of the atmosphere, there is also an apparent loss of both sucrose and fibre for which no explanation has yet been found. N. Deerr<sup>5</sup> records experiments tending

<sup>1</sup> *Int. Sugar J.*, 1945, 47, 102; *B.*, 1945, III, 120.

<sup>2</sup> *Rept. 63rd Meet. Hawaiian Sugar Planters Assoc.*; *Int. Sugar J.*, 1945, 47, 166; *B.*, 1945, III, 165.

<sup>3</sup> *Proc. 1943 Meet. British West Indies Sugar Assoc.*; *Int. Sugar J.*, 1945, 47, 184.

<sup>4</sup> *Int. Sugar J.*, 1945, 47, 176; *B.*, 1945, III, 203.

<sup>5</sup> *Ibid.*, 269; *B.*, 1945, I, 386.



to show that the rate of settling of coarse suspensoids is influenced by the precipitation within the system of magnesia derived from the introduction of soluble magnesium salts, and he suggests that this observation may find application in the clarification of cane juices.

Attention has been directed to the collection and utilisation of sugar cane wax which is concentrated in the filter-press cake. C. Venkatarao and M. Narsingarao,<sup>6</sup> using methyl ethyl ketone, have separated cane wax into 43% of soluble fatty matter of m.p. 53.5° and 57% of insoluble matter of m.p. 81.5° with almost all the sterol present in the wax contained in the fraction of lower melting point. R. T. Balch and C. B. Broeg<sup>7</sup> have made a study of various solvents used for extracting the wax; they find that petroleum naphthas of b.p. 85—120° are most suitable. For the separation of wax of high melting point they have used acetone and methyl ethyl ketone, the latter being more efficient in the removal of fatty matter but at the same time dissolving more material of high melting point.

J. C. Gonzalez Maiz<sup>8</sup> has examined the dehydration of molasses at atmospheric pressure and finds a loss of 23.37% of the reducing sugars. On the other hand, when the dehydration is effected under a vacuum of 27 inches, R. D. Lamie, M. Moore, C. F. Bonilla, and E. J. Gealy<sup>9</sup> find no loss, but state that the process is of interest to distillers only in the absence of tank steamers, though offering a source of stock feed to farmers.

#### BEET SUGAR MANUFACTURE.

In last year's Report (p. 388) mention was made of the Vallez process of beet juice purification through a system of ion interchange. D. Gutleben and F. Harvey<sup>10</sup> have afforded more details of the process as carried on at Mount Pleasant factory in Michigan, U.S.A. They record purities in the treated material of 98.9 as compared with an initial purity of 91.6; the ash is reported as reduced from 0.370% to 0.035%, indicating a reduction of over 90%. L. Lang<sup>11</sup> has commented on the process and calls attention to the low pH, 2.5, in the effluent from the ash-absorbing tank where, although the temperature is reduced to 20° and the time of exposure to a minimum, some inversion must take place. He asks for figures of yield before and after the installation of the process as well as for the fuel figures consequent on a dilution from 13° to 10.4° Brix or to nearly 30%; for the cost of a unit capable of removing 1000 kg. of ash before regeneration he gives 16,000 dollars. The Wintzall-Lauritzson process now in use in nineteen beet sugar factories in Sweden is discussed

<sup>6</sup> *Proc. 12th Ann. Conv. Sugar Tech. Assoc. India*, 191; *Int. Sugar J.*, 1945, 47, 183; B., 1945, III, 121.

<sup>7</sup> *Sugar Bull.*, 1944, 22, 117, 123, 171; B., 1945, III, 164.

<sup>8</sup> *Proc. 17th Meet. Assoc. Tech. Azuc. Cuba*; *Int. Sugar J.*, 1945, 47, 107; B., 1945, III, 120.

<sup>9</sup> *Sugar*, 1944, 39, No. 8, 26; *Int. Sugar J.*, 1945, 47, 165; B., 1945, III, 165.

<sup>10</sup> *Int. Sugar J.*, 1945, 47, 11; B., 1945, III, 58.

<sup>11</sup> *Ibid.*, 12; B., 1945, III, 58.



by A. Backman.<sup>12</sup> In this process the diffusion battery waste waters after mechanical separation of the suspended matters are mixed with the pulp press waters which have been treated with sulphuric acid to pH 3.2; by this means the proteins are coagulated and are removed in specially designed tanks. The combined waters are then returned to the diffusion battery and there is no excess effluent. The protein material collected is mixed with molasses and pulp to form a balanced ration for stock comparable in feeding value to oats. Difficulties due to the circulation of acid water, including both corrosion and loss of sugar due to inversion, have not been found to be serious.

J. C. Macdonald<sup>13</sup> challenges the results obtained in Sweden with the Wintzall-Lauritzson process. He had used an essentially similar process twelve years ago and found both corrosion and loss of sugar. He considers that the method of sterilisation by heat, neutralisation with lime, and minimum time in circulation is the best method of re-using process waters in the beet sugar factory.

H. C. Millar<sup>14</sup> describes the use of ammoniated beet pulp obtained by the exposure of the pulp to ammonia at a pressure of 175 lb. per sq. in., when an edible product containing 4% of nitrogen results. The production of calcium citrate and of calcium gluconate from beet molasses has been studied by O. Roberts and D. Murphy.<sup>15</sup> They make use of an *Aspergillus*, using sphagnum moss or sawdust as a fermentation base. The results were satisfactory and afforded a yield of 25—30 g. of citrate and 40—45 g. of gluconate from 200 g. of molasses.

J. C. Macdonald<sup>16</sup> calls attention to the acceptance by chemists of an "unknown loss" of sugar, which may amount to as much as 0.3% or to 900 tons of sugar in the treatment of a crop of 300,000 tons of roots; he thinks that this loss is capable of correction by more careful control on operation.

#### SUGAR REFINING.

The question whether the original producer should make a raw or a refined sugar is as old as the industry. Originally the factories in the Mediterranean area established after 800 A.D. through Arab expansion produced a white refined sugar, and it was not until the fifteenth century that Venetian industrialists initiated the importation and refining of raw sugars. Later refining interests in Europe were able to influence tariff legislation so that the original producers were compelled to import only material of lower grade and suited for refining. Lately, and very largely due to the use of vegetable carbons, refining at site has been practised. A very detailed analysis of the methods to be employed has

<sup>12</sup> *Int. Sugar J.*, 1945, 47, 72; *B.*, 1945, III, 120.

<sup>13</sup> *Ibid.*, 100; *B.*, 1945, III, 121.

<sup>14</sup> *Proc. Amer. Soc. Sugar Beet Tech., Third Meet.*, 529; *Int. Sugar J.*, 1945, 47, 19; *B.*, 1945, III, 64.

<sup>15</sup> *Sci. Proc. Roy. Dublin Soc.*, 1945, 23, 307; *Int. Sugar J.*, 1945, 47, 207.

<sup>16</sup> *Int. Sugar J.*, 1945, 47, 236; *B.*, 1945, III, 224.



been made by J. C. Macdonald<sup>17</sup> for both beet and cane sugars. He discusses the subject from both the economic and technical points of view, and concludes that the dominant factor is the market immediately available for a sugar refined at site.

H. C. de Whalley<sup>18</sup> has examined the cause of an alleged "putrefaction" of golden syrup associated with the appearance of black patches on the contents of the tins. He finds the reason to be the exposure of the steel plate followed by the formation of an iron compound of hydroxy-acids produced by the action of iron and oxygen on the reducing sugars in the presence of slight acidity. Such syrups are quite wholesome and should not be condemned as food.

#### ANALYSIS.

F. W. Zerban and J. Martin<sup>19</sup> have redetermined the refractive indices of dextrose and of invert sugar, using the Bausch and Lomb sodium light instrument.<sup>20</sup> Up to a concentration of 45% of dextrose they find slightly lower results than those recorded by Körner, Reischel, and Höppner,<sup>21</sup> with a reverse condition up to 80%, when agreement is found.

M. Shoikhet<sup>22</sup> finds that small quantities of reducing sugars in granulated sugars can be determined by the use of Nessler's solution, the coloration produced being compared with that recorded in a chart made under standardised conditions.

B. K. Singh, S. Prasad, and A. Chandra<sup>23</sup> propose to determine the percentage of sucrose in white sugars from observation of the viscosity of the material before and after inversion.

A. H. Edwards<sup>24</sup> describes a method of determining sulphates in sugar products by titration with barium chloride, the position of complete precipitation of the sulphate ion being shown by a change in colour from brown to orange in the presence of tetrahydroxybenzoquinone. P. Malvezin<sup>25</sup> has simplified the method of Bertrand for the determination of reducing sugars by titrating directly against a standardised solution of cupric sulphate in ammonia and eliminating the vacuum filtration and titration against permanganate.

S. G. Smart and T. J. Mitchell<sup>26</sup> have studied the determination of water in sugars using the vacuum oven and also drying at atmospheric pressure; results obtained by the former procedure were more regular

<sup>17</sup> *Int. Sugar J.*, 1944, **46**, 294; 1945, **47**, 40; B., 1945, III, 38, 73.

<sup>18</sup> *Analyst*, 1944, **69**, 242; B., 1944, III, 204.

<sup>19</sup> *J. Assoc. Off. Agric. Chem.*, 1944, **27**, 295; B., 1945, III, 13.

<sup>20</sup> Straat and Forrest, *J. Opt. Soc. Amer.*, 1939, **29**, 240.

<sup>21</sup> *Z. Ver. deut. Zuckerind.*, 1901, **51**, 409.

<sup>22</sup> *Sborn. Rabat Kiev*, 1940, 233.

<sup>23</sup> *Proc. 12th Conv. Sugar Tech. Assoc. India*, I, p. 173; *Int. Sugar J.*, 1945, **47**, 162; C., 1945, 178.

<sup>24</sup> *Proc. Amer. Soc. Sugar Beet Tech., Third Meet.*, 541; *Int. Sugar J.*, 1945, **47**, 245; C., 1945, 252.

<sup>25</sup> *Bull. Assoc. Chim. Sucr.*, 1942, **59**, 498; *Int. Sugar J.*, 1945, **47**, 163.

<sup>26</sup> *Int. Sugar J.*, 1945, **47**, 68; C., 1945, 115.



than by the latter. They conclude, however, that the water content of raw sugars obtained by steam oven heating cannot even be regarded as comparative from one sugar to another.

C. A. Fort and S. Byall<sup>27</sup> have discussed the relative value of reporting ash in sugar products as carbonate or as sulphate. They point out that there can be no single relationship connecting the two systems; with the salts present originally in the form of phosphate or sulphate the carbonate and sulphate ash may be nearly equal, but with the salts present in organic combination the sulphate ash may be as much as 20% in excess of the carbonate ash.

#### BONE BLACK.

V. R. Deitz has reported on the preliminary work done by the (U.S.) National Bureau of Standards.<sup>28</sup> It was found in the first place that the quantity of gas adsorbed was proportional to the extent of surface, which might vary from 17 to 130 sq. m. per g., dependent on how long the bone black had been in service. This simple relation was not found to hold with colour adsorption. The causes in the difference in behaviour were found to be firstly in the diffusion of the liquor itself into the pore space, and in the competition of all constituents for surface including the sugar itself and the water; additional factors not yet examined were probably the pH effect of the char, the influence of colloids and suspended matter, and the nature of the constituents.

A. B. Babcock<sup>29</sup> has examined the ageing of bone black on the basis of porosity as determined by the weight per cubic foot of the material. He finds a definite relation between porosity and colour removed, a black originally weighing 38 lb. per cubic foot becoming spent and inoperative when the weight had increased to 99.8 lb. As a measure of the adsorption effected by a black he heats the material after use to a temperature of 1000° F. and collects the gases given off, the volume of which he finds is proportional to the amount of colour removed.<sup>30</sup>

#### SUGAR AS RAW MATERIAL.

There have been a few developments in the use of sugar as a plastic agent, the use of which dates back to 1939.<sup>31</sup> No further development has yet been reported in the use of Sucrolite,<sup>32</sup> one form of which prepared from sucrose, formaldehyde, and urea still remains in the laboratory or semi-manufacturing stage. Sucrose acetate is, however, now prepared by British Celanese Ltd., by a process giving a yield of 80% of the theoretical,<sup>33</sup> and glucose appears among the materials which when esterified

<sup>27</sup> *Proc. Amer. Soc. Beet Sugar Tech., Third Meet.*, 489; B., 1945, III, 204.

<sup>28</sup> *Int. Sugar J.*, 1945, 47, 99; cf. A., 1943, I, 225.

<sup>29</sup> *Ibid.*, 128, 209; B., 1945, III, 184.

<sup>30</sup> *Ibid.*, 104; B., 1945, I, 347.

<sup>31</sup> C. Böhler, G.P. 552,380 of 1929.

<sup>32</sup> F. M. Hesse, *Brit. Plastics*, 1935, 6, 503.

<sup>33</sup> B.P. 552,161; B., 1943, II, 209.



with  $\alpha$ -chloroacrylic acid and polymerised affords a material which can be used in the manufacture of safety glass.<sup>34</sup>

Considerable interest attaches to the use of bagasse, the fibrous residue left after milling sugar cane, and essentially to that portion derived from the soft interior parenchyma. It is used in two ways: in the production of a resin and in the manufacture of a filler, the latter of which when used in conjunction with the bagasse resin has been found to be superior to wood flour.<sup>35</sup> A further development has been the manufacture of a thermoplastic resin from bagasse, commercial production having begun in 1944. An alcohol-soluble bagasse resin has also been made, as well as a water-soluble thermosetting bonding resin adapted for use with paper, cloth, and veneers. There appear to be prospects of the successful use of this and of similar materials in the manufacture of buttons, knobs, dashboards, etc. in the automobile industry, and in the manufacture generally of radio and electrical equipment as well as in the building and furniture industry.<sup>36</sup>

<sup>34</sup> U.S.P. 2,388,967.

<sup>35</sup> *Int. Sugar J.*, 1945, 47, 267.

<sup>36</sup> *Ibid.*, 268.



# STARCHES.

BY J. A. RADLEY, M.Sc., F.R.I.C.

THE recent work on starch has been reviewed by K. H. Meyer,<sup>1</sup> and T. J. Schoch<sup>2</sup> has given an excellent account of the fractionation of starch by the older and the newer methods together with the properties, structures, and functions of the fractions so obtained.

The sources and characteristics of glutinous ("waxy") starches are discussed by M. M. MacMasters and G. E. Hilbert,<sup>3</sup> who compare the composition of waxy with that of normal grains for maize and sorghum varieties. The glutinous variety of grains, in general, contain more oil and protein but less starch than the normal varieties. Normal processing methods can be used to obtain glutinous starch but some varieties of sorghum give rise to difficulties due to pigmentation and, in general, glutinous starches are more susceptible to changes in processing conditions. Their use in industry as a replacement for tapioca starch is discussed. As a new source of starch which is somewhat similar to maize starch in its characteristics, C. B. Patel<sup>4</sup> has examined *Panicum miliaceum*. Treating this corn in the same way as maize, 52% of starch is obtained and the waste bran, containing 11.4% of protein matter, is a good cattle food.

A. L. Shewfelt and G. A. Adams<sup>5</sup> describe a method of separating wheat starch from gluten which yields 93% of the starch with a gluten content of 0.4—0.5% and 96% of the gluten containing 10—12% of starch. After kneading the flour with water (0.8 part) for 20 minutes it is slurried with 3.3 parts of water and passed to a shaker sieve with a 17XXX silk screen. Starch is recovered from the liquid passing through whilst the crude gluten, tailing over, is extruded through a fine perforated plate, washed with a little water, screened, and dried. A plant for continuous large-scale operations is described.

According to M. M. MacMasters and G. E. Hilbert<sup>6</sup> ageing does not affect the quality of starch prepared from wheat stored for lengths of time up to 15 years, although the amount recovered is reduced by storage. Wheat damaged by heat-treatment, however, is unfit for use in starch production.

A. H. Kelling<sup>7</sup> describes a process for the manufacture of maize starch in which the processing water is repeatedly separated and returned to

<sup>1</sup> *Textilber.*, 1943, 24, 125; B., 1945, III, 73.

<sup>2</sup> "Advances in Carbohydrate Chemistry," Academic Press Inc., New York, 1945, p. 247.

<sup>3</sup> *Ind. Eng. Chem.*, 1944, 36, 958; B., 1945, III, 38.

<sup>4</sup> *Current Sci.*, 1943, 12, 325; B., 1944, III, 230.

<sup>5</sup> *Canad. Chem.*, 1944, 28, 502; B., 1944, III, 230.

<sup>6</sup> *Cereal Chem.*, 1944, 21, 258; B., 1945, III, 14.

<sup>7</sup> U.S.P. 2,324,849-50 and 2,325,250; B., 1945, III, 185.



the flow at a different stage of the process each time, thus leading to a conservation of water and a consequent building-up of the dissolved solids in the liquor; fresh water is introduced only in the last stage of purification of the starch. The addition of sodium benzoate or benzoic acid to the steep-water used in maize starch manufacture is claimed, by J. P. Bishop and W. F. Henry,<sup>8</sup> to minimise thinning of the starch by bacterial or enzymic agencies which would produce acid if not so treated.

A. Peltzer and A. Peltzer, jun.,<sup>9</sup> also build up the concentrations of the separated constituents by dewatering the mill starch and repulping the cake for centrifugal separation into a starch underflow and a gluten overflow. The latter contains a high percentage of gluten and is in part dewatered with further mill starch and in part used for repulping.

G. A. Adams, G. A. Ledingham, and N. H. Grace<sup>10,11</sup> prepare starch from wheat flour by kneading it in an oscillating hemi-cylindrical vessel fitted with an adjustable, free-swinging, rubber-covered roller while washing in a stream of water. Recovery of 95—97% of starch and 95% of gluten is claimed, the starch content of the gluten being about 10%. The length of the washing period is the most important factor in this method; increasing the washing time from 45 to 90 minutes decreases the starch content of the gluten from 7.3 to 0.8%. A centrifugal process, requiring only a relatively small number of screens, is described by A. Peltzer.<sup>12</sup> M. M. MacMasters and G. E. Hilbert<sup>13</sup> find the "amylo-dextrin" fraction of wheat flour, which tails over in starch-tabling, consists of the smallest starch granules, in an ungelatinised condition, and large, gelatinised, damaged granules (87—94%) together with protein, pentosans, fat, ash, and cellulose (1—2, 4, 0.7, 0.3, and about 3% respectively). The small-granule starch fraction is viscous and semi-fluid, probably because of the electroviscous effect of large sorptive surfaces of the small granules and high ash content.

The same workers, with M. J. Cox,<sup>14</sup> have shown that sulphur dioxide in maize steeping, by virtue of its reducing action, peptises and disintegrates the protein matrix enclosing the starch granules, the effect increasing with temperature (38—55°) and sulphur dioxide concentration (0.0—0.4%).

R. O. McCoy<sup>15</sup> carries out the steeping, in the presence of sulphur dioxide, with water to which the water-soluble maize constituents have been added. The gluten-settling water, for example, is mixed with the steep-water, obtained earlier, to give sp. gr. 1.3—2.0° B. This procedure, it is claimed, increases the paste viscosity of the starch so prepared.

<sup>8</sup> U.S.P. 2,322,413; B., 1945, III, 142.

<sup>9</sup> U.S.P. 2,186,037; B., 1945, III, 59.

<sup>10</sup> *Canad. J. Res.*, 1945, 23, F, 143; B., 1945, III, 144.

<sup>11</sup> *Ibid.*, 155; B., 1945, III, 144.

<sup>12</sup> U.S.P. 2,323,077; B., 1945, III, 142.

<sup>13</sup> *Cereal Chem.*, 1944, 21, 548; B., 1945, III, 124.

<sup>14</sup> *Ibid.*, 540; B., 1945, III, 74.

<sup>15</sup> U.S.P. 2,186,303; B., 1945, III, 59.



A modified refining process, using specially designed brushing sieves, is described by F. M. Smith.<sup>16</sup>

In the preparation of starch from wheat and other cereals, R. J. Dimler, H. A. Davis, C. E. Rist, and G. E. Hilbert find that the maximum dispersion of protein occurs at pH 10.5—11.8 (obtained by the use of sodium hydroxide), the temperature not being above 35°. Barley, rye, oat, maize, sorghum, and rice flours were not so satisfactory as wheat flours for use in this process. By tabling the starch dispersion some 70—80% of finest quality starch with not more than 0.3% protein content is obtained. Centrifuging the starch dispersion yields all the starch in one fraction of 94—98%, containing 0.4—0.6% of protein; the product is suitable for wet processes not requiring the highest quality starch.

### ETHERS AND ESTERS.

R. L. Whistler<sup>18</sup> has reviewed the preparation and properties of starch esters and, in conjunction with G. E. Hilbert,<sup>19</sup> finds that amylose triacetate from chloroform solution readily forms films, of good tensile strength and elongation characteristics, which compare favourably with those of commercial cellulose acetate. Owing to its greater inherent plasticity it requires only 10—20% of plasticiser, *e.g.*, dibutyl phthalate, as against 20—40% required by commercial cellulose triacetates. Amylopectin triacetate, like the triacetate of whole starch, gives weak and brittle films. F. Höppler<sup>20</sup> has examined the properties and possible uses of sodium amylopectin glycollate. It is water-soluble, its aqueous solutions have very high viscosities, and it is non-toxic as it is unaffected by a passage through the alimentary canal. Höppler discusses, at length, its suitability as a gelatin substitute in bacteriological media, its use in jams, baking, ice-cream, salad dressings, milk products, gums, and cosmetics, for egg-preserving, and for tablet making.

Water-soluble  $\beta$ -carboxyethyl starch ethers are obtained by L. H. Bock and A. L. Houk<sup>21</sup> by suspending raw, gelatinised, or solubilised starch, which has undergone no appreciable degradation, in 1—10% caustic alkali at 0—60°, using 0.025—2.0 mols. of the alkali per glucose unit of starch. To the mixture are added 0.1—1.5 mols. of acrylonitrile per glucose unit, the reaction time being dependent on the temperature and on the concentration of acrylonitrile. Some 5—6 hours are required to obtain a water-soluble product when 0.1—0.5 mol. is used. The various ethers are used as textile sizing and coating agents and as pigment-binders in textile printing. Syrups that can be used as plasticisers are obtained by S. M. Cantor<sup>21</sup> by treating starch with alcohols containing

<sup>16</sup> U.S.P. 2,320,755; B., 1945, III, 74.

<sup>17</sup> *Cereal Chem.*, 1944, 21, 430; B., 1945, III, 58.

<sup>18</sup> "Advances in Carbohydrate Chemistry," Academic Press Inc., New York, 1945, p. 279.

<sup>19</sup> *Ind. Eng. Chem.*, 1944, 36, 796; B., 1945, III, 14.

<sup>20</sup> *Chem.-Ztg.*, 1943, 67, 72; B., 1945, III, 14.

<sup>21</sup> B.P. 564,585; U.S.P. 2,316,128-9; B., 1945, III, 14, 39.



hydrochloric acid and 5% of water. Methyl alcohol gives a product containing 80% of  $\alpha$ -methylglucoside whilst ethyl, iso- or normal propyl or butyl alcohol, or amyl alcohol gives products containing the corresponding glucosides.

E. A. Talley and L. T. Smith<sup>22</sup> described the acetylation of starch with keten in glacial acetic acid, using sulphuric acid as a catalyst, the product having an acetyl value of 42.5%. The preparation of soluble allylstarch by refluxing starch acetate and allyl bromide in acetone-50% aqueous caustic soda for 3½ hours has been described by R. E. Nichols, R. M. Hamilton, L. T. Smith, and E. Yanovsky,<sup>23</sup> who further describe its uses in lacquers, for coating and impregnating paper or textiles, and other industrial applications.

### MODIFIED STARCHES.

To produce starch of low viscosity and a low content of water-soluble matter, Staley Manufacturing Co.<sup>24</sup> treat an aqueous suspension of native starch at 35–65°, and pH 5–7, with not more than 2.4% of mineral acid and 0.04–2.5% of a chromium compound, *e.g.*, chromium trioxide, until all the chromium is reduced (10 minutes to 6 hours or more) and then recover and dry the starch; the fluidity of the pasted starch can be predicted from the amount of chromium used and should the modified, but unpasted, starch be rendered alkaline (pH 7–9) immediately before adjusting to pH 5–7, it yields fluid pastes in water, independent of the pH.

A product, resembling raw starch under the microscope but giving, on prolonged cooking with water, a short, smooth paste of stable viscosity, is prepared by A. D. Fuller<sup>25</sup> by treating an aqueous suspension of raw starch with an oxidising compound, *e.g.*, sodium hypochlorite, in presence of a reaction inhibitor such as urea, acetamide, ammonia, potassium cyanide or thiocyanate, aniline, phenol, etc.; in one example sodium hypochlorite, giving 0.5% of available chlorine on the weight of starch, is allowed to act in the presence of 0.5% of urea.

H. H. Schopmeyer and G. E. Felton<sup>26</sup> modify waxy starches from maize or other source by mixing with aqueous acid at pH about 2 (1–4) and heating at temperatures up to 60° until it gives the desired alkali fluidity test between the values of 20 and 96. The mixture is then neutralised and the starch separated, washed, and dried. The product gives a reddish-brown iodine test, has high adhesive strength as shown by the pick test, and shows no tendency to reversion. The alkali-fluidity and the pick tests are described.

<sup>21</sup> *Ind. y Quim.*, 1942, 4, 1; B., 1945, III, 166.

<sup>22</sup> *J. Org. Chem.*, 1945, 10, 101; A., 1945, II, 269.

<sup>23</sup> *Ind. Eng. Chem.*, 1945, 37, 201; B., 1945, III, 122.

<sup>24</sup> B.P. 570,364; B., 1945, III, 205.

<sup>25</sup> U.S.P. 2,317,752; B., 1945, III, 74.

<sup>26</sup> U.S.P. 2,319,637; B., 1945, III, 74.



Corn Products Refining Co.<sup>27</sup> modify root starches in such a way that the hot and cold viscosities are reduced, allowing the production of a gel of desirable properties which can be used in pie-fillings and dessert powders. They allow the starch, with or without acid pretreatment, to react with 0.075—0.5% of its weight of formaldehyde or acetaldehyde in aqueous suspension at pH 1.6—2.5; pH, temperature, time of treatment, and amount of aldehyde are all adjusted to give the desired degree of change. The pH is then adjusted to between 5.8 and 6.8 by the addition of, e.g., caustic soda and the filtered starch is resuspended in a solution of ammonium or alkali sulphite or bisulphite, sufficient to react with any free aldehyde, after which the product is filtered, washed, and dried.

#### PHYSICAL PROPERTIES.

M. Sameč,<sup>28</sup> continuing his series of papers on the physical and chemical characteristics of starch, reviews the recent work on the nature of the water-absorption and thermal effects on hydration of starch, changes in starch on drying, determination of water in starch, and the sedimentation of starch suspensions with reference to manufacturing processes. The swelling of starches, especially barley starch, in aqueous sodium salicylate has been examined by G. Lejeune,<sup>29</sup> who finds that swelling is not affected by pH but may be inhibited by organic liquids such as ethyl alcohol or acetone; removal of calcium from the starch assists the process.

#### PHYSICAL TESTING.

Evaluation of the water-resistance of starches used in paper coating work is carried out by C. C. Kesler and E. T. Hjemstad<sup>30</sup> by dipping a 50-w. 110-v. electric light bulb into the coating mix, drying, and then switching on the current for a definite period, the maximum temperature attained being not above 125°. The bulb is then attached to a variable-speed motor by means of a Gooch crucible adaptor, and rotated against a circular brush immersed in 300 c.c. of clear, cold water for a definite time interval, e.g., 10 minutes. The turbidity of the water, measured nephelometrically, is inversely proportional to the water-resistance. By measuring manometrically the change of volume of an inflated gas-bag, which takes place after dipping it in a coating mixture and drying under appropriate conditions, they obtain the formula  $s = 0.6845 - 0.67 \log v$ , where  $v$  = change in volume of the bag due to the drying of the film, to express the shrinkage ( $s$ ) of the film on drying.

The amylograph, a torsion viscometer recording the resistance to shear offered by a suspension, has been widely used in the baking industry and for examining the pasting properties of starch. C. A. Anker and W. F. Geddes<sup>31</sup> find, by its use, that the swelling of starch is a first-order,

<sup>27</sup> B.P. 566,236; B., 1945, III, 59.

<sup>28</sup> *Kolloid-Beih.*, 1943, 54, 435; B., 1945, III, 122.

<sup>29</sup> *Compt. rend.*, 1943, 216, 217; B., 1945, III, 122.

<sup>30</sup> *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 160; C., 1945, 171.

<sup>31</sup> *Cereal Chem.*, 1944, 21, 335; B., 1945, III, 99.



and granule disintegration a second- or higher-order, reaction; as starch concentration increases maximum paste viscosity increases, temperature of transition and paste temperature at maximum viscosity fall, and the rate of post-maximal decrease becomes greater. Maximum viscosity decreases as the pH is increased from 5.2 to 6.7, a greater decrease being caused by citrate than by bimalate buffer. They also use the instrument to examine the effect on viscosity of enzyme action, the influence of the variety of wheat used in preparing the starch, the efficiency of cold gelatinising agents, and the effect of acid modification or chlorination. The microscopy of wheat, rye, barley, oat, rice, and maize starches has been dealt with by F. D. Armitage<sup>32</sup> in a series of articles illustrated by photomicrographs.

#### ANALYSIS.

Degradation products of starch, *e.g.*, mono- to tetra-saccharides, have been separated and quantitatively analysed by A. Tiselius and L. Hahn<sup>33</sup> by absorption on charcoal. The absorbant was pretreated with a dilute solution of ephedrine to prevent losses and to increase the absorption affinities of the components of the mixture; a more concentrated solution of the drug was used as a displacement developer. In their study of the different dextrans obtained by the action of amylase on maize and potato starches they found that malt amylase on maize starch produced a trisaccharide only. Two dextrans from potato starch were found to contain tri-, penta-, and hexa-saccharides and the proportion of each present was determined.

A stable starch indicator solution for use in iodometric titrations is described by W. S. Platner,<sup>34</sup> and H. A. Conner and R. W. Bovik<sup>35</sup> have suggested the use of a solubilised starch, made by ball-milling starch in alcohol until disintegrated, drying, and regrinding, which is added as a powder near the end-point of the iodometric titration.

J. P. Nielson and P. C. Gleason,<sup>36</sup> in an extension of Nielson's work on the colorimetric determination of starch by the iodine method,<sup>37</sup> take into account the different intensities of the starch-iodide colours produced by starches from different sources. They obtain the "apparent starch" content by colorimetric means and then derive factors for converting these starch values into the equivalent values for potato starch. Good agreement between the corrected values for starches from various sources by the colorimetric method and the values determined by enzymic hydrolysis was obtained.

A modified colorimetric starch-iodide method is described by H. Rath, D. Keppler, and I. Roesling<sup>38</sup> for evaluating desizing materials. The

<sup>32</sup> *Ind. Chem.*, 1943, **19**, 131, 195, 234, 301, 360, 412; B., 1945, III, 75.

<sup>33</sup> *Kolloid-Z.*, 1943, **105**, 177; C., 1944, 178.

<sup>34</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 369; C., 1944, 186.

<sup>35</sup> *Ibid.*, 772; C., 1945, 146.

<sup>36</sup> *Ibid.*, 1945, **17**, 131; C., 1945, 179.

<sup>37</sup> *Ibid.*, 1943, **15**, 176; A., 1943, III, 539.

<sup>38</sup> *Textilber.*, 1944, **25**, 18, 58; C., 1945, 27.



rate of action, as distinct from the total activity, is indicated by comparing curves obtained by plotting the colour, obtained under standard conditions, against the time to attain it for both the sample and an equal weight of a standard enzyme preparation. A similar testing method using the actual sized fabric is less reliable.

The effect of certain preservatives on the determination of starch by the diastase method has been examined by C. F. Poc and B. P. Jukkola,<sup>39</sup> who find that the starch recovery is decreased by the addition of more than 2 g. of sodium chloride to a 3-g. sample and is 87.4% when 5 g. are added. Potassium nitrate, boric acid, and borax have little effect, but sodium bisulphite or salicylate has some detrimental effect when more than 2 g. are used. Sodium benzoate has the largest effect, giving a recovery of 80% when more than 3 g. are used.

According to M. P. Etheredge,<sup>40</sup> a collaborative study of the Hopkins (Mannich-Lenz) polarimetric method with the hydrochloric acid-diastase procedure indicates that the former is as good as, if not better than, any other known method. Calcium chloride is not an ideal dispersion medium and the glucose-starch factor of 0.9 is too low. F. R. Earle and R. T. Milner<sup>41</sup> use calcium chloride as the dispersing medium for maize, wheat, tapioca, and potato starches and find that, after correcting for non-starch constituents, all samples have  $[\alpha]_D + 203^\circ$ . E. T. Steiner and J. D. Guthrie<sup>42</sup> extract the starch from plant materials with ammonium carbonate, twice precipitate with iodine-potassium iodide, followed by treatment with sodium thiosulphate, wash the precipitate with 70% alcohol, and dissolve in calcium chloride solution; after precipitating the proteins with uranyl acetate the starch is determined polarimetrically. The method is claimed to give truer values for starch content than either the Hopkins method or the malt-diastase method.

#### DEXTRINS.

L. T. Smith and S. G. Morris<sup>43</sup> have investigated the absorption of dry hydrochloric acid gas by starch of varying moisture content. As the latter decreases from 12% the gas absorbed falls, but its penetration into the starch mass increases. With a moisture content of 3—4% sufficient penetration and absorption occur to permit dextrinisation to proceed, so that by choosing suitable time and temperature conditions dextrins with high viscosity and low sugar content can be produced. W. S. Bowen<sup>44</sup> induces dextrinisation of partly gelatinised potatoes by mixing with a slightly acid salt mixture and drying, the product being claimed as a flour improver and yeast activator. A suitable salt mixture comprises ammonium chloride 8%, sodium chloride 20%, calcium dihydrogen phosphate 62%, and calcium sulphate 10%.

<sup>39</sup> *Food Res.*, 1944, 9, 338; C., 1945, 35.

<sup>40</sup> *J. Assoc. Off. Agric. Chem.*, 1944, 27, 404; C., 1945, 38.

<sup>41</sup> *Cereal Chem.*, 1944, 21, 567; C., 1945, 116.

<sup>42</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 736; C., 1945, 119.

<sup>43</sup> *Ind. Eng. Chem.*, 1944, 36, 1052; B., 1945, III, 39.

<sup>44</sup> U.S.P. 2,185,368; B., 1945, III, 39.



## THE FERMENTATION INDUSTRIES.

BY J. L. SHIMWELL, D.Sc., F.R.I.C., AND M. HORWOOD, Ph.D., A.R.I.C.

### BARLEY AND MALT.

THE arguments for and against the use of the combine harvester are fully discussed in various papers, and informed opinion seems to be definitely in favour of its use. Its main disadvantage lies in the fact that the crop has to be dried in specially constructed farm dryers, with resultant risk to the germinative capacity of the grain. If the maltsters can be reasonably certain that the barley coming to them has been correctly treated on the farm, the question whether to combine or not would appear to be chiefly an economic one. L. R. Bishop<sup>1</sup> contributes a very informative paper, which emphasises the superiority of the combine in this respect, at least as far as harvesting is concerned. Unfortunately, no indication is given of the costs of farm drying; more information on this point would be welcome.

The use of farm dryers makes a rapid determination of the germinative capacity of barley very necessary, and L. R. Bishop<sup>2</sup> has continued the studies on this question begun in 1944.<sup>3</sup> He determines the germinative capacity by peeling the soaked grains and allowing them to germinate on sand. By this method a result can be obtained in 24—48 hours, and he suggests<sup>4</sup> that such a test should be carried out on all barleys that have been farm-dried; barleys with less than 95% of sound, viable corns should be rejected. The same author<sup>2</sup> has also attempted to find a quicker method of estimating germinative capacity, and concludes that staining the germ-ends of cut barley grains with biselenite solution gives promising results when compared with the germination method; moreover, the result can be obtained in about three hours. However, the method needs more extensive trial before a final opinion can be expressed as to its value. The paper concludes with some very interesting observations of the "germinative energy" of thirteen varieties of barley, which go a long way to confirm the author's hypothesis that there is a relationship between the degree of dormancy of a barley and its malting, as distinct from brewing, quality.

G. D. H. Bell<sup>5</sup> gives an account of the work done at Cambridge which resulted in the introduction of the new variety barley known as Pioneer. This is a two-row winter hardy hybrid obtained by crossing Spratt-Archer with Tschermak, a Bavarian two-row winter hardy variety; the new

<sup>1</sup> *J. Inst. Brew.*, 1945, 51, 127.

<sup>2</sup> *Ibid.*, 215; B., 1945, III, 247.

<sup>3</sup> *Ibid.*, 1944, 50, 166; B., 1944, III, 205.

<sup>4</sup> *Ibid.*, 1945, 51, 166; B., 1945, III, 224.

<sup>5</sup> *J. Agric. Sci.*, 1944, 34, 223; B., 1945, III, 87.



hybrid possesses ideal qualities for autumn-sown malting barley, being slow-maturing and giving a high yield. An interesting feature of the new barley is the fact that its winter hardiness is more strongly shown than in its Tschermak parent. So far no results have been published dealing with field and brewing trials of the new variety; these are awaited with interest. Some account of the complexities and difficulties encountered in making a new variety of barley available to growers is given by H. Hunter.<sup>6</sup>

J. A. Anderson<sup>7</sup> contributes an informative review of the research work done in Canada on malting barley. The barley variety O.A.C. 21 is taken as a standard, and "unknown" varieties are grown side by side with it at various stations all over the country under widely differing environments. Samples are then submitted for malting under standard conditions in small-scale laboratory maltings. The steep tank and germinating chamber are capable of dealing with 24 samples simultaneously and the kiln with 12. Methods of working are given in the original paper, together with detailed diagrams of the plant used. The author goes on to discuss the results obtained; thus, malt extract is related to barley extract and barley starch, and inversely to the cellulose-lignin fraction. Besides high extract, however, high enzymic activity is desirable owing to the short time of germination used in Canada and the extensive use of starch adjuncts. In this respect there is a high positive correlation between the enzymic activity of a barley and its malt.

In a further paper, the same author<sup>8</sup> discusses the relationship between nitrogen content and malting quality, and shows that the relationships deduced by L. R. Bishop for two-rowed varieties hold also for Canadian six-rowed varieties. There is a close relationship between barley-protein and wort-nitrogen, starch-liquefying power, proteolytic activity, and malting loss, but an inverse correlation with malt extract. Low-nitrogen barleys give mellow malts with high extract, but they require a longer time on the floor due to low enzymic activity.

W. O. S. Meredith and H. R. Sallans<sup>9</sup> discuss the same topics after having analysed 144 barleys, their malts, and their worts. They conclude that wort quality depends on the amounts of extract and enzymes produced during malting, rather than on extract and  $\beta$ -amylase in the barley. Despite the close relationship between malt extract and the starch and the extract of barley, and between the Lintner value of malt and that of barley after papain extraction, no wort quality is significantly related to these three barley qualities. Thus, wort quality cannot be adequately assessed by a determination of Lintner value, extract, and wort-nitrogen on the malt, though these figures will be useful indications of what to expect.

<sup>6</sup> *J. Inst. Brew.*, 1945, 51, 189.

<sup>7</sup> *Wallerstein Lab. Comm.*, 1945, 8, 5; B., 1945, III, 166.

<sup>8</sup> *Ibid.*, 1944, 7, 179; B., 1945, III, 100.

<sup>9</sup> *Canad. J. Res.*, 1945, 23, F, 132; B., 1945, III, 142.



The results of field and brewing trials of two barleys, Oderbrücker and Wisconsin Barbless (Ped 38), are described in the report of the Malt Research Institute, U.S.A.<sup>10</sup> The latter malt proved to be very similar to the standard O.A.C. 21, but the Oderbrücker malt was higher in nitrogen and diastatic power.

### HOPS.

In view of the frequently expressed opinion that Great Britain lags behind the U.S.A. in the application of research to industry, it is refreshing to find that the editor of the well-known *Wallerstein Laboratory Communications* considers that the reverse is often the case, at least in the matter of hop research. That this is so is due to the work of the Wye-East Malling research team, which has been ably summarised by F. H. Beard.<sup>11</sup> He describes the early work undertaken at Wye, and summarises the work of E. S. Salmon on the propagation of new varieties of hops, nine of which are now grown commercially, all having a higher preservative value than the older English varieties, whilst three, Brewers' Gold, Bullion Hop, and Brewers' Stand-by, surpass the best American growths available in the British market. The remainder of the paper is devoted to a brief description of the various processes involved in growing hops for brewing. W. G. Keyworth,<sup>12</sup> in a companion paper, discusses the present state of our knowledge with regard to hop diseases. Of some 20 distinct diseases which affect hops in this country, only five, mould, downy mildew, *Verticillium* wilt, nettlehead, and mosaic, are of general importance. Of these, the first two can be controlled by certain cultural measures combined with the use of sprays. *Verticillium* wilt, first discovered in a Kent garden in 1924, is more difficult to eradicate. There appear to be two types of outbreak, fluctuating and progressive; the former has very little effect on the crop, but the latter renders the area derelict, and very drastic measures are necessary to check it. Some success has been achieved in checking new outbreaks by means of hygiene and soil disinfection, but the chief hope would seem to be in the growth of strains resistant to *Verticillium* infection. With regard to nettlehead and mosaic, which are virus diseases, the author recommends firstly the use of healthy stock, and secondly the removal of all plants showing even the slightest symptoms.

E. S. Salmon,<sup>13</sup> in his 28th annual report on the trial of new varieties of hops examined in 1944, considers that the rainfall in the early part of the year was too small for the production of very heavy crops. Nevertheless, one new late variety, EE 69, cropped at the rate of 26½ cwt. per acre, whilst the average yields at East Malling are 25¾ cwt. per acre for Brewers' Gold over 16 years, and 26 cwt. per acre for Bullion Hop over 10 years. Two of the new hops, a mid-season variety, OJ 47, and

<sup>10</sup> *Malt Res. Inst., Publ. No. 4*, 1944; *J. Inst. Brew.*, 1945, 51, 196.

<sup>11</sup> *Wallerstein Lab. Comm.*, 1945, 8, 83.

<sup>12</sup> *Ibid.*, 99.

<sup>13</sup> *J. Inst. Brew.*, 1945, 51, 224; *B.*, 1945, III, 248.



a late variety, OR 55, show some resistance to *Verticillium* wilt, as well as giving a high yield per acre and a satisfactory soft resin content. Two other varieties, the John Ford hop and Northern Brewer, are reported to have excellent keeping qualities, and in the opinion of the author are likely to replace the Golding varieties "Cobb's" and "Tutsham," on account of their far higher brewing value and immunity from mosaic disease. It is interesting to note that for the tenth consecutive year, OM 26, a bud sport of the "Nonsuch hop," showed a higher percentage of soft resins than its parent.

Some of the hops resistant to *Verticillium* wilt have been submitted to brewing trials by L. C. Thompson and B. M. Brown,<sup>14</sup> who report favourably on the following types: Beltring varieties 1140 and 1147, Wye varieties OB 53 (the "Nonsuch" hop), OJ 47, and OR 55. Of the other Wye varieties tested, AEE 55, OM 26, AOX 19, and AOY 18 were considered suitable for blending off with other hops. OB 53 and OM 26 had been reported on favourably previously after brewing trials, by J. S. Ford.<sup>15</sup> L. Fletcher<sup>16</sup> reports good results with three other new varieties raised by E. S. Salmon, namely, OM 103, T 8, and WFC 81 (Wye Field Golding); the last-named is one of the four seedlings from the "Canterbury Golding" crossed with a male hop seedling of "Brewers' Gold," as are "Northern Brewer" and the "John Ford hop."

D. E. Bullis and G. Alderton<sup>17</sup> have examined the colorimetric method for the measurement of soft resins in hops first put forward by Guthrie and Philip. They conclude that  $\alpha$ -resin can be estimated by measuring the intensity of colour produced by adding 2% uranyl nitrate solution in methyl alcohol to a light petroleum extract of the hop under investigation. The  $\beta$ -resin is determined by subtracting the percentage of  $\alpha$ -resin from the total petroleum ether extractives. The preservative value, calculated on the basis of  $P.V. = 10(\alpha + \beta/3)$ , agreed very well with that obtained by gravimetric methods. The authors are also of the opinion that light petroleum is preferable as a solvent to methyl alcohol for the gravimetric estimation of  $\alpha$ -resin in old hops.

F. Rabak<sup>18</sup> suggests that the aroma of hops, usually completely lost by evaporation from the copper, may be successfully imparted to beer by the addition of hop oil extract of fresh or recently dried hops in alcoholic solution. It is almost certain, however, that the Excise authorities would frown on any such addition in this country.

#### BIOCHEMISTRY. STARCH, CEREALS, AND ENZYMES.

W. Z. Hassid<sup>19</sup> contributes a very informative article dealing with the modern conception of the starch complex. He discusses very lucidly

<sup>14</sup> *J. Inst. Brew.*, 1945, 51, 39; B., 1945, III, 74.

<sup>15</sup> *Ibid.*, 1936, 42, 352; 1942, 48, 136.

<sup>16</sup> *Ibid.*, 1945, 51, 232; B., 1945, III, 248.

<sup>17</sup> *Wallerstein Lab. Comm.*, 1945, 8, 118; B., 1945, III, 252.

<sup>18</sup> *Ibid.*, 1944, 7, 173; B., 1945, III, 100.

<sup>19</sup> *Ibid.*, 1945, 8, 34.



the views of the Haworth-Hirst, Meyer, and Freudenberg schools, and shows how the action of  $\alpha$ - and  $\beta$ -amylases on starch may be explained by means of Meyer's conception of the structure of amylopectin and amylose.

R. L. Whistler and G. E. Hilbert<sup>20</sup> report that amylose and amylopectin fractions of potato, wheat, tapioca, and maize starches may be separated by precipitation of the amylose with  $\alpha$ -nitropropane under conditions similar to those used for separation by butanol.  $\beta$ -Nitropropane gave slightly higher yields of amylose from maize; nitroethane gave lower results. R. W. Kerr and O. R. Trubell<sup>21</sup> propose to measure the amount of amylose and amylopectin in starch by a spectrographic method depending on the different light transmissions of these fractions when stained with iodine.

K. Myrbäck<sup>22</sup> and his co-workers publish a number of papers dealing with the preparation of various dextrans from starch and the action of amylases on them.

E. Kneen<sup>23</sup> has made a study of the amylase system of sorghum malt, and found that it contains large amounts of an  $\alpha$ -amylase and a relatively minute amount of  $\beta$ -amylase, which was, however, sufficient to influence greatly the post-dextrinisation saccharification of starch. The  $\alpha$ - and  $\beta$ -amylases of sorghum malt were similar in properties to the  $\alpha$ - and  $\beta$ -amylases of barley malt respectively. Prolonged action of the sorghum malts gave as high a saccharification as that brought about by barley malt; this observation emphasises the inadequacy of the Lintner and similar methods which evaluate the  $\beta$  component of malts only.

J. Davidson<sup>24</sup> has measured the free and total amylase content of various cereals by extraction with water and 0.5% papain solution respectively. He finds that the total is always greater than the free amylase in barley, wheat, and rye, but the papain has no effect on soya beans or cereals with a low content of free amylase. The consistent differences found between free and total amylase in one variety as compared with another of the same species of wheat, barley, and rye support the view that differences in amylase content represent varietal differences.

C. E. Weill and M. L. Caldwell<sup>25</sup> have studied the  $\beta$ -amylase of barley, and their results support the view that the thiol group and free tyrosine are necessary for its action. The amylase is slowly inactivated by nitrous acid, due to the oxidation of the thiol groups present, but in the early stages this inactivation is reversible by hydrogen sulphide. Subsequently the inactivation is not reversible, due to the destruction of tyrosine. The same authors, together with R. S. Weil,<sup>26</sup> have examined pancreatic

<sup>20</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 1161; A., 1945, II, 392.

<sup>21</sup> *Paper Trade J.*, 1943, **117**, *TAPPI Sect.*, 161; B., 1946, III, 133; C., 1946, 90.

<sup>22</sup> *Biochem. Z.*, 1941-42, **311**, 213, 242, 227, 234; A., 1945, III, 55.

<sup>23</sup> *Cereal Chem.*, 1945, **22**, 112; B., 1945, III, 185.

<sup>24</sup> *J. Agric. Res.*, 1945, **70**, 175; A., 1945, III, 648.

<sup>25</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 212, 214; A., 1945, III, 479.

<sup>26</sup> *Ibid.*, 1079; A., 1945, III, 888.



amylase in a similar way, and show that it requires free primary amino-groups, though these are of no importance to  $\beta$ -amylase of barley. On the other hand, free thiol and tyrosine groups are apparently unimportant to the action of pancreatic amylase.

W. W. Pigman<sup>27</sup> has determined the extent of hydrolysis of starch by various amylases in the presence and absence of yeasts. With cereal  $\alpha$ -amylases or *Aspergillus* amylase complete conversion into fermentable material occurred in the presence, but not in the absence, of yeasts. Only partial conversion is obtained by the action of pancreatic and *Bac. mesentericus* amylases, and with wheat and soya-bean  $\beta$ -amylases.

D. J. D. Hockenfull and D. Herbert<sup>28</sup> have examined the amylase and maltase of *Clostridium acetobutylicum*. The maltase differs from that of yeast in having a more acid pH optimum (4.5) and appears to be a specific maltase rather than an  $\alpha$ -glucosidase. The amylase has a pH optimum of 4.8, and converts starch quantitatively into maltose.

L. D. Beckford, E. Kneen, and K. H. Lewis<sup>29</sup> report on the characteristics of the amylases from 16 varieties of *B. subtilis* or *B. mesentericus*.

H. K. Archbold and C. Datta<sup>30</sup> have examined sugar metabolism in the barley stem in relation to ear development. The results obtained indicate that the starch in the ear is not derived from the free sugars in the stem, and their loss is a senile change and not a movement controlled by growth demands of the ear. The results are further discussed and summarised by H. K. Archbold.<sup>31</sup>

O. Quensel<sup>32</sup> has used the ultra-centrifuge to study the globulins of barley, which can be separated into four fractions by its use. The molecular weights of the  $\alpha$  and  $\gamma$  fractions are 26,000 and 166,000 respectively, whilst those of the  $\beta$  and  $\delta$  fractions, although not determined accurately, are about 100,000 and 300,000 respectively.

#### BEER AND THE BREWING PROCESS.

S. Laufer<sup>33</sup> discusses the types of water met with in breweries and how they may be modified by suitable treatment to serve various purposes. C. Enders<sup>34</sup> has found that first wort contains barley-fat to the extent of 7 p.p.m., and as it has a marked foam-reducing effect, the author proposes that it should be removed from the wort, and suggests methods for doing this.

A. J. C. Cosbie<sup>35</sup> discusses the problems of beer pasteurisation and the various types of pasteuriser available commercially. A useful review

<sup>27</sup> *J. Res. Nat. Bur. Stand.*, 1944, **33**, 105; A., 1945, III, 196; C., 1945, 116.

<sup>28</sup> *Biochem. J.*, 1945, **39**, 102; A., 1945, III, 479.

<sup>29</sup> *Ind. Eng. Chem.*, 1945, **37**, 692; A., 1945, III, 691.

<sup>30</sup> *Ann. Bot.*, 1944, **8**, 363; A., 1945, III, 206.

<sup>31</sup> *Nature*, 1945, **156**, 70.

<sup>32</sup> *Thesis, Uppsala*, 1942; A., 1945, II, 176.

<sup>33</sup> *Brewers' Digest*, Jan., 1945, 36; *J. Inst. Brew.*, 1945, **51**, 143.

<sup>34</sup> *Woch. Brau.*, 1942, **59**, 161; *J. Inst. Brew.*, 1945, **51**, 197.

<sup>35</sup> *J. Inst. Brew.*, 1945, **51**, 233; B., 1945, III, 248.



of pasteurisation, apart from the common mistake of attributing to beer-spoilage bacteria the ability to form heat-resistant spores.

The electron microscope has been used to examine beer deposits by G. L. Clark and J. W. Lawrie.<sup>36</sup> The work is as yet in an elementary stage, but one feature of interest which emerges is that the proportion of larger-sized proteins in sediments increases with age, which seems to indicate that polymerisation is occurring.

A. H. Warth<sup>37</sup> considers that when a beer is naturally conditioned over a long period, the gas absorbed by the beer is not freely released, possibly because it is in loose combination with the proteins. Artificially carbonated beers are, however, much less retentive, with resultant deficiency of foam-retaining qualities. On long storage part of the "free" carbon dioxide becomes converted into the "bound" type.

#### YEAST AND THE BIOCHEMISTRY OF FERMENTATION.

E. A. V. Montgomery and J. White<sup>38</sup> have determined the water content of the yeast cell by an ingenious method depending on the dilution effect brought about by the water in pressed yeast external to the cell when mixed with a peptone solution of known strength. It was found that the average water content of the cells of 16 samples of bakers' pressed yeast was 63.6%, with variations of  $\pm 3\%$ . The authors show that total moisture content of yeast is not a true guide to its consistency, which depends on the distribution of the water inside and outside the cell. The amount of water inside the cell can be varied by chemical agents, such as salts, which plasmolyse it, whilst dilute ammonia results in the increase of internal water, with maximum effect at pH 8.7. A similar increase takes place when the cell is treated with dilute hydrochloric and sulphuric acids, with maximum absorption at pH 1.5 and pH 1.8 respectively. The yeast cell is able to combine with albumin on the acid side of the isoelectric point of the latter, due to the fact that the yeast cell bears a negative charge, as has been shown by cataphoresis experiments.

R. S. W. Thorne<sup>39</sup> continues his studies of the nitrogen metabolism of yeast. He shows that from a binary mixture of nitrogen nutrients containing ammonia and amino-nitrogen, the former is assimilated in the earliest stages of growth in preference to the latter, but thereafter they are assimilated simultaneously at rates which are strictly proportional to one another. When the two nutrients are initially present in equivalent concentrations, the rate at which amino-nitrogen is assimilated is a characteristic of the particular amino-acid used. Thus, alanine contributes only 19% of the total nitrogen assimilated from an alanine-ammonium phosphate mixture, whereas asparagine contributes 68% from an asparagine-ammonium phosphate mixture. The nitrogen

<sup>36</sup> *Wallerstein Lab. Comm.*, 1944, 7, 79; B., 1945, III, 15.

<sup>37</sup> *Amer. Brewer*, 1944, 77, Dec., 25; B., 1945, III, 123.

<sup>38</sup> *J. Inst. Brew.*, 1945, 51, 279; B., 1946, III, 47.

<sup>39</sup> *Ibid.*, 6; A., 1945, III, 401.



content of growing yeast increases rapidly to about double its normal value in the initial phase of growth, and thereafter gradually falls until the growth has finished. A point which emerges from the results is that a considerable proportion of the nitrogen assimilated is excreted back into the medium (about 15% in the experiments described) probably as polypeptides, and this proportion increases as the fermentation proceeds. The same author<sup>40</sup> in a further paper summarises much of his previous work on this subject in a very clear and interesting manner.

R. J. Winzler, D. Burk, and V. du Vigneaud<sup>41</sup> have studied the effect of biotin on *Saccharomyces cerevisiae*, both alone and in combination with various sources of nitrogen. Biotin-deficient yeasts respired and fermented at one twentieth to one tenth the rate of normal yeast, but on addition of biotin in the presence of ammonia, the rate of fermentation gradually rose, followed by an increase in the rates of respiration and finally growth. Other nitrogen sources, particularly asparagine, arginine, and urea, could be substituted for ammonia, but were far less effective. Utilisation of biotin by yeast was markedly decreased in the absence of glucose or phosphate.

C. C. Lindegren<sup>42</sup> discusses the possibility of improving industrial yeasts by selection or hybridisation. It is now known that most industrial yeasts are heterozygous, and it would appear feasible to produce new hybrids having the desirable characteristics of both parents by mating two haploid cells of different strains; thus a haploid lactose-fermenter mated with a haploid maltose-fermenter might produce a hybrid capable of fermenting both. Unfortunately, haploid colonies, if kept as such for any length of time, lose their power to copulate, becoming typical examples of *Torulæ*, so that selection and hybridisation are mutually exclusive. Haplophase yeasts are in general not sufficiently stable to permit their use industrially, but it is possible to use them providing that cultural conditions are chosen so that undesirable mutants are suppressed as far as possible.

Pyrophosphatase, an enzyme capable of hydrolysing pyrophosphate to orthophosphate, which had previously been isolated from various seeds and bottom yeast, has now been isolated from bakers' yeast by K. Bailey and E. C. Webb.<sup>43</sup> Its activity is dependent on the thiol grouping specifically activated by magnesium ions.

R. Nilsson<sup>44</sup> discusses the differences of behaviour of living yeast, dried yeast, and cell-free yeast juice in fermentation. The fermentative power of dried yeast may be partly or totally inhibited by the addition of certain substances, such as organic solvents, saponins, or zymase poisons such as sodium fluoride. The author believes that this is due not

<sup>40</sup> *J. Inst. Brew.*, 1945, 51, 114; A., 1945, III, 570.

<sup>41</sup> *Arch. Biochem.*, 1944, 5, 25; A., 1945, III, 256.

<sup>42</sup> *Wallerstein Lab. Comm.*, 1944, 7, 153; B., 1945, III, 100.

<sup>43</sup> *Biochem. J.*, 1944, 38, 394; A., 1945, III, 129.

<sup>44</sup> *Naturwiss.*, 1943, 31, 25; A., 1944, III, 768.



to the disruption of the zymase system, but rather to the destruction of a regulatory water-insoluble lipoid, thought to be present in living or dried yeast, but not in maceration juice. It is believed to function by virtue of its being a dephosphorylating enzyme.

V. Bergmann<sup>45</sup> has estimated the phosphate content of wort at various stages during its fermentation by yeast, and concludes that there is a relationship between nuclear division and phosphate content; the rise and fall of the latter correspond with the release of phosphate into the wort on nuclear division, and its subsequent uptake for intense vegetative growth.

The continuing scarcity of high-grade protein in present-day diets is the cause of the great interest evinced during the past year in yeast as a foodstuff. A. C. Thaysen<sup>46</sup> makes the point that given adequate nutrients, half a ton of yeast can produce 245 tons of protein in 24 hours from inorganic nitrogen, a protein synthesis 144,000 times as fast as that possible by a half-ton bullock. In normal times the sugar could be supplied from various sources which previously were run to waste.

J. J. Stubbs, W. M. Noble, and J. C. Lewis<sup>47</sup> have obtained yields of 42—58 g. of dry yeast (*Torula utilis*) from 100 g. of sugar using syrups of prunes, figs, or raisins, and the press-juices of apples, pears, or peaches, as nutrient media; somewhat higher yields were obtained in a works pilot plant. W. H. Peterson, J. F. Snell, and W. C. Frazier<sup>48</sup> have worked out the conditions suitable for the production of fodder yeast from wood sugars; the yield is 35—40% of the total reducing sugars present.

H. Fink<sup>49</sup> considers that yeast-protein, although having as high a biological value as the best plant-protein, is not as good as animal protein due to cystine deficiency; this can be remedied by the addition of keratin decomposition products. J. Grossfeld and H. Hess<sup>50</sup> have measured the fat content of food yeast by extraction of the fatty materials with solvents after treatment with hydrochloric acid; they find that the average amount of fat and phosphatide from 4 samples was 9.8% on a moisture-free basis.

#### MICROBIOLOGY.

T. K. Walker and J. Tösić,<sup>51</sup> in the course of their studies on organisms of the genus *Acetobacter*, have examined the characteristics of a species isolated from ropy beer which corresponds very closely to *A. viscosum* Shimwell (Baker, Day, and Hulton), and also another species isolated from the pitching yeast of a London brewery which corresponds very closely to the Lister Institute culture labelled *A. aceti* (Hansen) Holland.

<sup>45</sup> *Amer. Brewer*, 1945, **78**, 17; B., 1946, III, 8.

<sup>46</sup> *J. Soc. Arts*, 1945, **93**, 353; B., 1945, III, 166.

<sup>47</sup> *Food Ind.*, 1944, **16**, No. 9, 68; B., 1945, III, 59.

<sup>48</sup> *Ind. Eng. Chem.*, 1945, **37**, 30; B., 1945, III, 123.

<sup>49</sup> *Woch. Brau.*, 1944, **61**, 1; A., 1944, III, 670.

<sup>50</sup> *Z. Unters. Lebensm.*, 1943, **85**, 32; C., 1945, 182.

<sup>51</sup> *J. Inst. Brew.*, 1945, **51**, 245; B., 1945, III, 248.



The former, when first isolated, was capable of growing in pasteurised beer with strong pellicle formation which tended to submerge and was decidedly ropy. Two years later it was found that the surface growth took the form of a friable film, whilst the deposit was not ropy but tended to adhere in a firm layer to the bottom of the tube. The organism is more aërobic than *A. turbidans*, *A. mobile*, or *A. acetosum*. *A. aceti* similarly lost its power to form a pellicle in pasteurised beer two years after its initial isolation.

W. J. Nickerson, jun.,<sup>52</sup> has found that the causative organism in the souring of a sample of red wine was a new species of *Zygosaccharomyces* which he designates *Z. acidifaciens*; its outstanding physiological characteristic is its ability to transform glucose into acetic acid. A full description of the organism is given in the original paper.

J. B. Rehm, M. Sommer, and V. Ellerbusch<sup>53</sup> are of the opinion that metal barrels are superior to wooden ones from the point of view of the subsequent biological stability of the beer they contain, an opinion which should be widely shared by brewers in this country. The wooden barrel is increasingly difficult to "sterilise" after repeated use, and unless lined with pitch, the organisms present in the wood will probably enter the beer. The authors state that the stability of draught beer is inversely related to the bacterial count of the rinsings of the barrel into which it is racked.

Attention is drawn by J. L. Shimwell<sup>54</sup> to the neglect of the use of the Gram stain in brewing bacteriology.

#### VITAMINS IN BEER AND BREWING MATERIALS.

Interest in the subject of vitamins in British beers has been well maintained during the past year. In addition to the thiamin and riboflavin previously reported, E. C. Barton-Wright<sup>55</sup> and F. W. Norris<sup>56,57</sup> report that nicotinic acid occurs in significant amounts in top-fermentation beers. The latter has estimated the nicotinic acid content of the usual raw materials used in brewing and of worts and beers prepared from them. Typical malting barleys contain from 80 to 150  $\mu\text{g}$ . per g., and the malts derived from them show a slightly higher figure (about 14% on the average). The amount present in sweet wort shows strong correlation with that in the malt from which it is derived, and the hops contribute a further small quantity. The late runnings from the mash-tun are relatively richer in nicotinic acid than would be expected on a gravity basis; this is in line with the findings of R. H. Hopkins and S. Wiener<sup>58</sup> with riboflavin. The yeast tends to withdraw nicotinic acid from the wort during fermentation, but this point is not definitely proved. The

<sup>52</sup> *Mycologia*, 1943, 35, 66; A., 1944, III, 292.

<sup>53</sup> *J. Bact.*, 1944, 47, 442; *J. Inst. Brew.*, 1945, 51, 51.

<sup>54</sup> *Wallerstein Lab. Comm.*, 1945, 8, 23; B., 1945, III, 166.

<sup>55</sup> *Biochem. J.*, 1944, 38, 314; C., 1945, 46.

<sup>56</sup> *J. Inst. Brew.*, 1945, 51, 38; B., 1945, III, 74.

<sup>57</sup> *Ibid.*, 177; B., 1945, III, 224.

<sup>58</sup> *Ibid.*, 34; B., 1945, III, 75.



average content of 20 samples of beer was 5.6 mg. per pint; roughly four pints of beer would supply the daily requirement of nicotinic acid for man. This finding is in agreement with that of E. C. Barton-Wright (*loc. cit.*), who has also shown that the vitamin is very stable, as is proved by the relatively large amounts in old beers.

R. H. Hopkins and S. Wiener<sup>58,59</sup> have continued their investigation into the occurrence of riboflavin in beer. They find that there is a considerable variation in the behaviour of brewery yeasts in fermentation; all produce riboflavin during growth, but whilst some secrete considerable quantities into the beer, others secrete some, and some none at all. The cause of this phenomenon is not known, although in general the more attenuative yeasts secrete more riboflavin. The normal processing of beer after fermentation does not appear to affect its riboflavin content adversely, but exposure of a pale beer to a very strong light for 28 hours caused a 30% loss of riboflavin.

J. W. Tullo and W. J. Stringer<sup>60</sup> confirm the findings of Hopkins and Wiener, but are of the opinion that the riboflavin in malt is readily extracted at 60° C., whereas the latter consider that adequate extraction is achieved only by sparging as in normal brewery practice. The whole subject of vitamins in top-fermentation beers is fully reviewed by R. H. Hopkins.<sup>61</sup>

J. G. Organ, E. M. James, and F. Wokes<sup>62</sup> find that there is an average loss of thiamin of 11.2% from barley on malting, but an average 15.7% gain during the brewing process for the manufacture of malt extract. Fourteen samples of malt extract had an average aneurin content of 131 i.u. per 100 g. of dry matter, whilst the nicotinic acid in 15 samples ranged from 7.5 to 13.4 mg. per 100 g.

P. R. Burkholder<sup>63</sup> has examined the seeds and sprouts (whole plant) of oats, wheat, barley, and maize for presence of the various constituents of the vitamin-B group, and finds that in each case there is an increase of all constituents on germination except in the case of thiamin, which remained approximately constant.

A. Hoffer, A. W. Alcock, and W. F. Geddes<sup>64</sup> discuss the factors affecting the fluorimetric method for the determination of riboflavin, and suggest a modified method for use with wheat and wheat products, whilst S. H. Rubin, E. de Ritter, R. L. Schuman, and J. C. Bauernfeind<sup>65</sup> show how the method may be used for the estimation of riboflavin in low-potency material.

E. H. Hoag, H. P. Sareth, and V. H. Cheldelin<sup>66</sup> report that they

<sup>59</sup> *J. Inst. Brew.*, 1945, **51**, 133; A., 1945, III, 570.

<sup>60</sup> *Ibid.*, 86; B., 1945, III, 123.

<sup>61</sup> *Wallerstein Lab. Comm.*, 1945, **8**, 110; B., 1945, III, 248.

<sup>62</sup> *Quart. J. Pharm.*, 1944, **17**, 183; B., 1945, III, 40.

<sup>63</sup> *Science*, 1943, **97**, 562; A., 1945, III, 43.

<sup>64</sup> *Cereal Chem.*, 1944, **21**, 515, 524; C., 1945, 121.

<sup>65</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 136; C., 1945, 185.

<sup>66</sup> *Ibid.*, 60; C., 1945, 122.



obtain more satisfactory results in the microbiological assay of pantothenic acid by using *Lactobacillus arabinosus* 17-5 than by using *L. casei*. The effective assay range for both organisms is 0.01—0.08  $\mu$ g. of pantothenic acid.

#### ANALYSIS.

The past year has seen the publication of the fourth edition of the "Methods of Analysis of the American Society of Brewing Chemists," a much revised and extended edition of that published in 1940. To the companion volume "Tables for Extract Determination in Malt and Cereals" has been added "Tables Related to Determinations on Wort, Beer, and Brewing Sugars and Syrups." The Methods volume is divided into eight main sections dealing with malt, cereal adjuncts, sugars and syrups, beer, hops, wort, yeast, and spent grains. The value of having standardised procedures for brewing analysis will be obvious to all, but the A.S.B.C. makes it clear that the methods given may be adapted to suit particular cases. It is obviously impossible to summarise even the main points of such a publication in this report; it has already been done by A. A. D. Comrie,<sup>67</sup> and the reader is referred to his summary. One or two comments may not be out of place, however. All determinations of specific gravity are made at 20° c. (68° F.), and in the authors' opinion this is preferable to the standard temperature of 15.5° c. (60° F.) used in this country. Laboratory temperature is almost always above the latter figure, and cooling liquids to it is a time-wasting procedure, necessitating as it does the use of ice during the summer months. Diastatic power of malt is expressed as "maltose equivalent" ( $4 \times$  degrees Lintner) and it is intended that the latter term should become obsolete. One point of criticism is that some of the determinations appear to demand an excessive degree of accuracy; thus malt colours are read to the nearest 0.1° on the Lovibond scale, whilst malt moistures, determined on the usual five-gram sample, are weighed to the nearest half-milligram.

Several papers have also appeared which deal independently with some of the methods given by the A.S.B.C. Thus, B. H. Nissen<sup>68</sup> has examined the methods available for measuring colour and turbidity in wort and beer. He considers that the Lovibond 52 series of glasses is not reliable owing to variations in duplicate glasses, and prefers standard colours made from Brand dyes. Allowance is made for the turbidity of the beer by adding suspensions of fuller's earth of known turbidity expressed as p.p.m. One difficulty encountered is that photoelectric measurements may or may not agree with the visual method due to variation in the type of haze (e.g., protein or dextrin haze) produced.

A collaborative investigation by a sub-committee of the A.S.B.C.<sup>69</sup> reports that chemical determination of the fermentable sugars in maize

<sup>67</sup> *J. Inst. Brew.*, 1945, **51**, 262.

<sup>68</sup> *J. Assoc. Off. Agric. Chem.*, 1944, **27**, 389; C., 1945, 36.

<sup>69</sup> *Brewers' Digest*, 1945, **20**, No. 5, 41; *J. Inst. Brew.*, 1945, **51**, 199.



syrups gives higher results than fermentation methods, due to the presence of reducing non-fermentable dextrins.

A. A. Bacher<sup>70</sup> reports the results obtained with several methods for the routine determination of total solids in yeast.

K. Whitehouse, A. Zarow, and H. Shay<sup>71</sup> recommend the adoption of a modification of the method of Scharrer and Kurschner for the estimation of crude fibre in distillers' dried grains. The reagent used for digesting the sample after removal of fat contains nitric and trichloroacetic acids in acetic acid. The method takes only half the time of the A.O.A.C. method; and the risk of error is minimised by the reduction of the number of transferences of the residue from five to three. H. W. Woodson and H. S. Mackenzie<sup>72</sup> describe an enzymic method for the estimation of fibre in maize which they consider could be adapted for use with other cereals.

W. J. Olsen, R. Evans, and A. D. Dickson<sup>73</sup> give details of a procedure for estimating the relative amounts of  $\alpha$ - and  $\beta$ -amylase present in malts. The method is a modification of that of Kneen and Sandstedt; the  $\alpha$ -amylase is estimated by observing the change of colour of the iodine reaction of the starch substrate in the presence of excess of  $\beta$ -amylase, converting the figure obtained into saccharifying equivalent, and subtracting this from total saccharifying activity. The difference represents  $\beta$ -amylase.

The method for the rapid estimation of starch based on colour development with iodine, proposed by J. P. Nielson,<sup>74</sup> has been modified and extended by the same author and P. C. Gleason.<sup>75</sup> Factors are given in the paper which enable the user of the method to convert colour intensity into weight of starch for various vegetables, using potato starch as the standard. The method has also been extended for use with dehydrated foods. A comparison with acid or enzymic hydrolysis methods showed very close agreement, although enzymic methods gave somewhat lower results.

K. A. Clendenning<sup>75</sup> has examined the factors affecting the accuracy of the estimation of starch in wheat by extraction with calcium chloride solutions.

L. E. Wise and J. W. Appling<sup>77</sup> describe a fermentation method for the estimation of *d*-xylose. Hexoses are first removed from the medium by the action of *Sacc. carlsbergensis*, and then the xylose by *Hansenula suaveolens*, which ferments xylose quantitatively, but not arabinose, rhamnose, fucose, or glucuronic acid. An accuracy of  $\pm 4\%$  is claimed.

<sup>70</sup> *Wallerstein Lab. Comm.*, 1944, **7**, 169; C., 1945, 125.

<sup>71</sup> *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 147; C., 1945, 179.

<sup>72</sup> *Cereal Chem.*, 1945, **22**, 158; C., 1945, 180.

<sup>73</sup> *Ibid.*, 1944, **21**, 533; C., 1945, 116.

<sup>74</sup> *Ind. Eng. Chem. [Anal.]*, 1943, **15**, 176; A., 1943, III, 539.

<sup>75</sup> *Ibid.*, 1945, **17**, 131; C., 1945, 179.

<sup>76</sup> *Canad. J. Res.*, 1945, **23**, B, 113; C., 1945, 255.

<sup>77</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 182; C., 1945, 178.



H. H. Browne<sup>78</sup> proposes to estimate maltose in the presence of glucose by a method which depends on the fact that glucose combines readily with bisulphite to become optically inactive, whereas maltose (and dextrans) are unaffected.

F. C. Hildebrand and R. C. Koehn<sup>79</sup> point out that relatively large errors occur in the estimation of proteins in cereals due to differences in sampling, screening, and grinding for analysis, as well as analytical error.

For those interested in methods of testing of brewers' pitch there is an interesting and informative paper by another Sub-committee of the A.S.B.C.<sup>80</sup>

Since the discovery that minute but regular traces of fluorine in human diet causes mottling of the teeth and stiffness of the joints, while larger doses may cause anaemia and skin and eye troubles, there has been a quickened interest in the estimation of this element in foodstuffs. H. E. Crossley<sup>81</sup> points out that barley contains 1—5 p.p.m. of fluorine, but this is not appreciably extracted in the wort, whereas adventitious fluorine derived from the coal used in kilning is almost entirely soluble in water. Analysis of many beers has shown that the fluorine content ranges from 0.4 to 1 p.p.m. approximately, and in the stronger beers brewed before the war it was possible that up to twice this amount of fluorine was present. As drinking water containing more than 1 p.p.m. may be detrimental to health, the author suggests that the coal used for kilning should be carefully selected, or screened to remove shaly matter. For those interested in the estimation of traces of fluorine, there is the method of the Society of Public Analysts,<sup>82</sup> or a modified procedure described by W. L. Lamar.<sup>83</sup>

L. V. Taylor<sup>84</sup> has examined various modifications of the Monier-Williams method for the estimation of sulphur dioxide in beer, but considers the original method the most satisfactory, and recommends its adoption as the official A.O.A.C. method.

The use of farm dryers in conjunction with combine harvesters makes pertinent the investigation of C. R. Jones and E. C. Dawson<sup>85</sup> into the arsenic content of grain dried directly with flue gas. They conclude that farm-dried grain is never likely to have an arsenic content greater than 1/30th of that of the fuel, and may reasonably be expected not to have more than 1/100th. Since coke, the solid fuel chiefly used in grain drying, does not usually appear to contain more than 40 p.p.m. of arsenic, that in farm-dried grain should not exceed 0.4 p.p.m. (1/350 grain per lb.).

<sup>78</sup> *Ind. Eng. Chem. [Anal.]*, 1944, 16, 582; C., 1945, 35.

<sup>79</sup> *Cereal Chem.*, 1944, 21, 370; C., 1945, 37.

<sup>80</sup> *Brewers' Digest*, 1944, 19, 40; *J. Inst. Brew.*, 1945, 51, 46.

<sup>81</sup> *J.S.C.I.*, 1944, 63, 343; B., 1945, I, 54.

<sup>82</sup> *Analyst*, 1944, 69, 243; C., 1944, 181.

<sup>83</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 148; C., 1945, 192.

<sup>84</sup> *J. Assoc. Off. Agric. Chem.*, 1944, 27, 386; C., 1945, 36.

<sup>85</sup> *Analyst*, 1945, 70, 256.



R. E. Essery<sup>86</sup> discusses the estimation of traces of metals in beer wort.

#### MISCELLANEOUS.

H. I. Rosenbloom<sup>87</sup> discusses the factors which should be considered in making up a detergent, and concludes that a satisfactory bottle-washing mixture is a mixture of various types of detergent.

S. I. Aronovsky, W. F. Talburt, and E. C. Lathrop<sup>88</sup> describe the preparation from glue, glucose, glycerin, and ground peanut hulls (hitherto a waste product) of "Noreseal," a new cork substitute. An advantage of this material is that its composition and physical properties may be controlled over a wide range.

#### OTHER FERMENTATION PROCESSES.

D. W. Steuart<sup>89</sup> reports that the amount of acetylmethylcarbinol in cider depends on the degree of acetification that has taken place; thus bottle ciders contain 1—5 mg. per 100 ml., whereas pricked ciders containing 0.3—1.5% of acetic acid contain 5—45 mg. per 100 ml.

R. E. O'Neill and A. M. Henry<sup>90</sup> have examined the method of Edwards and Nanji for distinguishing artificial from brewed vinegar, and put forward a modified method which they claim is more reliable. E. C. Barton-Wright<sup>55</sup> has analysed two vinegars for nicotinic acid content, and found that they contain 9.0 and 9.5  $\mu$ g. per g. respectively.

W. G. Artis and R. F. Bawden<sup>91</sup> have investigated the problems arising from the use of malt in industrial alcohol production. Their results show that the cooking stage cannot be eliminated, and that a minimum of 30 minutes' heating under 24 lb. gauge pressure must be used. Some malt must be added to the grain (maize) before cooking to liquefy the starch; maximum yields were obtained when this amount was 9% of the total malt, and when the total malt was approximately 20% of the total grain. When the malt used was 11.5% or more of the total grain, a wide range of malt diastatic power could be used (e.g., 144—207° Lintner), but at lower malt rates the diastatic power had a direct effect on the yield. Mash concentrations for maximum yields were 32—35 gals. per bushel of grain during conversion, and 38 during fermentation. Up to 16% of stillage (liquid from spent mashes) used after the cooking stage improved the yield.

L. J. Sciarini and J. C. Wirth<sup>92</sup> convert the pentoses present in wheat mashes hydrolysed with sulphuric acid by fermentation with *Fusaria*, yielding 6—12% of ethyl alcohol additional to that derived from the yeast fermentation. A similar process for fermentation of pentoses in mashes hydrolysed with hydrochloric acid has not yet been developed,

<sup>86</sup> *J. Inst. Brew.*, 1945, 51, 185; C., 1945, 252.

<sup>87</sup> *Amer. Brewer*, 1944, 77, No. 9, 21; B., 1945, III, 40.

<sup>88</sup> *Wallerstein Lab. Comm.*, 1944, 7, 101; B., 1945, II, 26.

<sup>89</sup> *Analyst*, 1944, 69, 307; B., 1945, III, 15; C., 1945, 36.

<sup>90</sup> *J. Assoc. Off. Agric. Chem.*, 1944, 27, 263; C., 1945, 37.

<sup>91</sup> *Cereal Chem.*, 1945, 22, 22; B., 1945, III, 167.

<sup>92</sup> *Ibid.*, 11; B., 1945, III, 167.



but yeast fermentation of such mashies yielded as much alcohol as did the combined fermentation of the sulphuric acid hydrolysates. An additional 13% of ethyl alcohol was obtained from industrial plant stillage by yeast fermentation following acid hydrolysis.

S. Laufer, E. D. Stewart, and L. T. Saletan<sup>93</sup> have compared the efficiency of mould amylase prepared from *Aspergillus oryzae* with barley malt for the saccharification of wheat mashies, using two methods of cooking, one involving autoclaving and the other (the atmospheric process) using a temperature not above 66° c. Saccharification was carried out using 8% of malt or 3% of mould bran. In the atmospheric process with mould bran the alcohol yield was 2—14% higher than with malt, but with pressure cooking the latter gave better results. Mould bran gave slightly better results with a saccharification temperature of 30° c. as compared with 52.5° c. in both processes. Malt saccharification at 57.5° c. was usually better than with mould bran at 52.5° or 30° in the pressure-cooking process, but poorer in the atmospheric process. Possible industrial advantages of the use of mould bran are the elimination of pressure cooking, lowering of saccharification temperature, and increased yields of alcohol.

L. C. Hao and J. A. Jump<sup>94</sup> have examined the possibility of using commercial mould and bacterial amylase preparations for the production of alcohol from maize. The bacterial amylases were used for the liquefaction of the mash, and the mould amylases for saccharification. The former gave satisfactory liquefaction, but the authors consider acid to be the most efficient liquefying agent. The conversion efficiency with mould amylases was higher than with malt, whilst a 1—2% increase of alcohol was obtained if approximately 60% of the mould was used for saccharification and the remainder added during fermentation.

E. C. Sherrard and F. W. Kressman<sup>95</sup> and W. L. Faith<sup>96</sup> discuss the economic prospects for the production of alcohol from wood sugars. H. C. E. Johnson<sup>97</sup> describes a modification of the Scholler process which yields 50—60 gals. and 30—40 gals. of alcohol per ton of conifer and hardwood respectively. R. H. Leonard and G. J. Hajny<sup>98</sup> use wood sugars for production of ethyl alcohol, using a fermentation with *Saccharomyces* spp. which is complete in 14—20 hours. This is achieved by the addition of reducing agents, or by heating the neutral hydrolysate at 140° c. for a short time. Steam-distillation of the hydrolysate to remove toxic substances is also beneficial.

The demand for synthetic rubber continues to stimulate interest in research into methods of production of  $\beta\gamma$ -butylene glycol. D. Perlman<sup>99</sup>

<sup>93</sup> *Ind. Eng. Chem.*, 1944, **36**, 811; B., 1945, III, 15.

<sup>94</sup> *Ibid.*, 1945, **37**, 521; B., 1945, III, 205.

<sup>95</sup> *Ibid.*, 5; B., 1945, III, 124.

<sup>96</sup> *Ibid.*, 9; B., 1945, III, 124.

<sup>97</sup> *Chem. Industries*, 1944, **55**, 226; B., 1944, III, 255.

<sup>98</sup> *Ind. Eng. Chem.*, 1945, **37**, 390; B., 1945, III, 206.

<sup>99</sup> *Ibid.*, 1944, **36**, 803; B., 1945, III, 16.



uses a fermentation of wood hydrolysates by *Aerobacter aerogenes*, in which wood sugars up to a concentration of 17% are completely fermented, about 35% of the sugar being converted into  $\beta\gamma$ -butylene glycol; some acetoin is also formed. A. J. Liebman<sup>100</sup> uses the same process, although he uses a sugar mash in place of wood hydrolysate. He points out that *A. aerogenes* produces the *d*- and the *meso*-forms of the diol, whereas *Aerobacillus polymyxa* produces only the *l*-diol together with relatively large amounts of ethyl alcohol, and is unprofitable unless the *l*-isomeride is specifically required.

G. A. Ledingham and G. A. Adams,<sup>101</sup> however, prefer *A. polymyxa*, as it is able to ferment starch directly. A cooked sterile mash of ground wheat is fermented at 32.5° c., the pH being kept in the neutral region by the addition of chalk or ammonia. The ratio of diol to alcohol formed varies with the method of working; thus it is four to one with aëration of the wort, but fermentation then requires 120 hours as against 72 when undisturbed, when the ratio is 1.3/1.0. Under optimum methods of working, a yield of 10 lb. of the diol and 6 lb. of alcohol is obtained from a bushel of wheat. The process is described in greater detail by various authors.<sup>102</sup>

T. M. Lees<sup>103</sup> considers that enzyme-converted starchy materials are unsatisfactory as fermentable substrates in the production of glycerol by the sulphite process, possibly because of the slow rate of fermentation of the maltose formed. Acid-hydrolysed maize products are more satisfactory, and it is possible to obtain yields of glycerol of over 30% using high concentrations of bisulphite and large yeast inocula. The strain of yeast used has little effect on yields from glucose or sucrose, but *Sacc. ellipsoideus* is best for fermenting maltose.

A. E. Williams<sup>104</sup> describes a process for the production of gluconic acid by fermentation with *Aspergillus niger*. The raw material is refined glucose with the addition of nutrient salts. The fermentation is allowed to run for approximately eight hours at 30° c., at the end of which time approximately 95% yield of gluconic acid is obtained. The mycelium is separated from the solution and retained in the fermenter for the next brew.

L. B. Lockwood and G. E. Ward<sup>105</sup> obtain itaconic acid (methylene-succinic acid) by fermentation in trays of 15% glucose solution by *Aspergillus terreus* at 30—32° c. at pH 2.0. The process yields about 25% by weight of itaconic acid, of which 80% is recoverable by crystallisation and the remainder by extraction with *n*-butyl alcohol. The product finds a use in the manufacture of plastics.

<sup>100</sup> *Oil and Soap*, 1945, 22, 31; B., 1945, III, 143.

<sup>101</sup> *Canad. Chem.*, 1944, 28, 742; B., 1945, III, 60.

<sup>102</sup> *Canad. J. Res.*, 1944, 22, C, 235, 241; 1945, 23, B, 1, 10; 23, F, 48, 72, 79; B., 1945, III, 142.

<sup>103</sup> *Iowa State Coll. J. Sci.*, 1944, 19, 38; B., 1945, III, 186.

<sup>104</sup> *Manufg. Chem.*, 1945, 16, 239; B., 1945, III, 206.

<sup>105</sup> *Ind. Eng. Chem.*, 1945, 37, 405; B., 1945, III, 206.



R. Arroyo<sup>106</sup> states that cultures of *Clostridium saccharobutyricum*, separated by enclosure in quartz tubes from mash fermenting with *Schizosacc. pombe*, activated the latter in a manner similar to that obtained when fermentation was carried out with mixed cultures of the two organisms. There was no activation when the bacteria were retained in glass tubes. The author considers that this observation supports the mitogenetic radiation theory of Gurwitsch.

A. N. Bindal and M. Sreenivasaya<sup>107</sup> have examined various raw materials for the production of amylase by *Aspergillus oryzae*; wheat bran and malt residues were most satisfactory, but both were greatly improved by the addition of 10% of ground-nut cake. The same authors<sup>108</sup> have determined the nitrogen requirements of *A. oryzae*. Inorganic nitrogen sources support both growth and enzyme production; of the amino-acids examined, asparagine gave the best, and glycine the poorest, production of amylase. With peptones, amylase production apparently depends both on the nature of the amino-acids constituting the molecule, and on the complexity of the latter, a peptic digest of fibrin being superior to any other peptone tested.

L. Kline, L. R. McDonnell, and H. Lineweaver<sup>109</sup> describe the use of juice from waste asparagus butts as the basis of a medium for the production of proteolytic enzymes from *Bacillus brevis* or *B. subtilis scaber*.

<sup>106</sup> *Sugar*, 1945, **40**, No. 1, 30; B., 1945, III, 166.

<sup>107</sup> *J. Sci. Ind. Res., India*, 1944, **3**, 245; 1945, **3**, 287; B., 1945, III, 74, 123.

<sup>108</sup> *Ibid.*, 386; B., 1945, III, 142.

<sup>109</sup> *Ind. Eng. Chem.*, 1944, **36**, 1152; B., 1945, III, 60.



## FOODS.

By E. B. HUGHES, D.Sc., F.R.I.C.

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### FEEDING STUFFS.

THE volume and diversity of the published work on the subjects of feeding stuffs and animal nutrition during the war period make one wonder how much of this material will be of permanent value. In this country agricultural research is well organised<sup>1</sup> and fundamental research has been proceeding concurrently with the *ad hoc* experiments necessary to solve temporary problems. There is also collaboration between this country and others in the British Commonwealth through the Imperial Agricultural Bureaux, but it seems incongruous to-day that, up to 1944 in U.S.A. and Australia and up to 1945 in Canada, investigations were proceeding regarding the utilisation of the wheat surplus for stock feeding.<sup>2</sup> In these studies it is noteworthy that the experience gained from experiments on humans with regard to the necessity for calcium supplements was applied. In the U.S.A. increasing attention is being given to the co-ordination of research on feeding stuffs.<sup>3</sup>

#### *General Nutritional Studies.*

The third (1945) edition of "Physiology of Farm Animals," by F. H. A. Marshall and E. T. Halnan,<sup>4</sup> fulfils its claim to be a guide to the modern science of animal nutrition. The Rowett Institute has contributed a

<sup>1</sup> "Agricultural Research in Great Britain." H. M. Stationery Office, *Cmd.* 6421, 1943.

<sup>2</sup> G. C. Griffiths, *J. Dept. Agric. Victoria*, 1942, **40**, 43; B., 1945, III, 173. M. Cullity and N. McKeown, *J. Dept. Agric. W. Australia*, 1944, **21**, 94; B., 1945, III, 173. A. C. T. Hewitt, *J. Dept. Agric. Victoria*, 1944, **42**, 97; B., 1945, III, 232. A. C. T. Hewitt and H. G. Turner, *ibid.*, 437; B., 1945, III, 232. G. A. Branaman, *Michigan Agric. Exp. Sta. Quart. Bull.*, 1944, **27**, 8. E. W. Crampton and G. C. Ashton, *Sci. Agric.*, 1945, **25**, 403; B., 1946, III, 117.

<sup>3</sup> O. H. Brownlee, "War-time Farm and Food Policy." V. Putting, "Dairying on a War Footing," Ames, Iowa, 1944. R. E. Buchanan, *J. Animal Sci.*, 1945, **4**, 87. H. C. McPhee, *ibid.*, 96.

<sup>4</sup> "Physiology of Farm Animals," Cambridge, 1945.



review on the water economy of farm animals,<sup>5</sup> and more details have been published of the work of the Agricultural Research Council Unit of Animal Physiology on ruminant digestion.<sup>6</sup> E. G. Hastings<sup>7</sup> has reviewed the microbiological aspects of this question. There have been studies from various angles of the effects of diet on carcass quality, e.g., the effects of plane of nutrition,<sup>8</sup> of mineral constituents,<sup>9</sup> and of pasture quality.<sup>10</sup> With pasture-fed animals the experimental difficulties are such that clear-cut results can hardly be expected, particularly in view of the variations in energy-output required to secure a given food intake.<sup>11</sup>

J. A. B. Smith<sup>12</sup> has briefly reviewed the literature up to 1943 on the effect of diet on lactation. Various studies on the values of specific diets have also been made.<sup>13</sup> K. L. Blaxter and T. H. French<sup>14</sup> have continued their work on the use of home-grown bulky foods for milk production, with particular reference to the effects of varying rates of feeding. Workers at the Cornell Agricultural Experimental Station<sup>15</sup> report that fat intake is positively correlated with milk yield.

Complete scientific control of stock feeding demands attention to both the major and the minor ingredients of the diet. Several attempts have been made to compound food supplements comprising liver and yeast preparations, leaf meals, etc., to satisfy the nutritive requirements of pigs and poultry at various stages of growth.<sup>16</sup> E. W. Crampton and J. M. Bell<sup>17</sup> found that chemical and digestibility data of typical Canadian pig feeds apparently failed to account for differences in animal response. F. B. Shorland and co-workers have studied the effect of various feed

<sup>5</sup> L. Leitch and J. S. Thomson, *Nutr. Abs. Rev.*, 1944, **14**, 197; A., 1945, **III**, 182.

<sup>6</sup> S. R. Elsdon, *J. Exp. Biol.*, 1945, **22**, 51. J. F. Danielli, M. W. S. Hitchcock, R. A. Marshall, and A. T. Phillipson, *ibid.*, 75.

<sup>7</sup> *Bact. Rev.*, 1944, **8**, 235; A., 1945, **III**, 404.

<sup>8</sup> D. M. S. Watson, *Empire J. Exp. Agric.*, 1943, **11**, No. 43/44, 191.

<sup>9</sup> J. L. Hall, H. W. Loy, D. L. Mackintosh, G. E. Vail, and C. E. Latschar, *Kansas Agric. Exp. Sta.*, 1944, *Tech. Bull.* 58.

<sup>10</sup> D. E. Walker and C. P. McMeekan, *New Zealand J. Sci. Tech.*, 1944, **26**, A, 99; B., 1945, **III**, 105. C. M. Kincaid, G. W. Litton, and R. E. Hunt, *J. Animal Sci.*, 1945, **4**, 164; B., 1946, **III**, 157.

<sup>11</sup> D. B. Johnstone-Wallace and K. Kennedy, *J. Agric. Sci.*, 1944, **34**, 190.

<sup>12</sup> *Proc. Nutrition Soc.*, 1944, **2**, 46; A., 1945, **III**, 301.

<sup>13</sup> A. A. Borland, A. L. Beam, and P. D. Jones, *Pennsylvania Agric. Exp. Sta.*, 1942, *Bull.* 424; B., 1945, **III**, 128. H. P. Davis and R. F. Morgan, *J. Dairy Sci.*, 1943, **26**, 625; B., 1945, **III**, 62. J. S. Moore and W. C. Cowser, *Mississippi Agric. Exp. Sta.*, 1943, *Bull.* 383; B., 1945, **III**, 128. R. G. Ritzman and N. F. Colovos, *New Hampshire Agric. Exp. Sta.*, 1943, *Tech. Bull.* 80. W. A. King, *New Jersey Agric. Exp. Sta.*, 1943, *Bull.* 704; B., 1945, **III**, 128. N. K. Williams, C. Y. Cannon, and D. L. Espe, *J. Dairy Sci.*, 1943, **26**, 241; B., 1945, **III**, 42.

<sup>14</sup> *J. Agric. Sci.*, 1944, **34**, 213, 217; A., 1945, **III**, 244.

<sup>15</sup> J. K. Loosli, L. A. Maynard, and H. L. Lucas, *Cornell Agric. Exp. Sta.*, 1944, *Mem.* 265; B., 1945, **III**, 255.

<sup>16</sup> V. F. McRoberts and A. G. Hogan, *J. Nutrition*, 1944, **28**, 165; A., 1945, **III**, 40. R. C. Miller, T. B. Keith, W. T. S. Thorp, and M. A. McCarty, *Pennsylvania Agric. Exp. Sta.*, 1943, *Bull.* 449; A., 1945, **III**, 243. A. G. Hogan and S. R. Johnson, *Missouri Agric. Exp. Sta.*, 1941, *Res. Bull.* 332; A., 1945, **III**, 625. D. M. Hegsted and F. J. Stare, *J. Nutrition*, 1945, **30**, 37; A., 1945, **III**, 769.

<sup>17</sup> *Sci. Agric.*, 1944, **25**, 43.



ingredients on the characteristics of the fat of the bacon pig,<sup>18</sup> and T. P. Hilditch and H. Jasperson<sup>19</sup> have produced further evidence concerning the constitution of the polyethenoid acids of the C<sub>18</sub> series in milk and grass fats.

E. T. Halnan<sup>20</sup> has determined the metabolisable energy values for poultry and rabbits of bran fractions milled under war-time conditions and has demonstrated that potato starch needs to be gelatinised before it can be digested by poultry. T. B. Mann<sup>21</sup> has suggested that high mortality in chicks may be due to the bacteriological condition of the protein ingredients or to feeding protein at too high a level, 14% being recommended instead of 20%, the level usually recommended. He also found that the fatty matter of certain fish and meat meals may completely or partially destroy vitamin-A; this observation may be compared with that of H. Patrick and C. L. Morgan<sup>22</sup> that the rôle of vitamin-E in chick nutrition is to stabilise vitamin-A or carotene.

Attention has been given in various quarters to the possibility of livestock being poisoned by weeds or shrubs which they might consume, General information on this subject has been published in Indiana, Australia, and East Africa.<sup>23</sup> Other contributions refer to stinkwort, ngaio, and algæ.<sup>24</sup> Fresh whole sugar beet may cause diarrhoea.<sup>25</sup> Spraying pastures with natural cryolites did not produce any ill effects on grazing stock.<sup>26</sup>

#### *Nitrogen Requirements.*

The utilisation of urea in the bovine rumen has been further studied by separating the bacterial matter synthesised; from analytical data this was considered comparable with linseed meal in nutritional value, and direct observations confirm this.<sup>27</sup> R. Braude, S. K. Kon, and E. G. White<sup>28</sup> have confirmed that yeast as a protein supplement for pigs may have a rachitogenic effect; it is also deficient in methionine

<sup>18</sup> F. B. Shorland, R. Hansen, and K. J. Hogan, *Empire J. Exp. Agric.*, 1944, **12**, 103. F. B. Shorland and P. B. D. de la Mare, *J. Agric. Sci.*, 1945, **35**, 33, 39; A., 1945, III, 302.

<sup>19</sup> *J.S.C.I.*, 1945, **64**, 109; A., 1945, III, 456.

<sup>20</sup> *J. Agric. Sci.*, 1944, **34**, 133, 139; B., 1945, III, 24.

<sup>21</sup> *Ibid.*, 1945, **35**, 95, 98, 108; A., 1945, III, 455. *Ibid.*, 207, 214; A., 1946, III, 320. *Ibid.*, 101; A., 1945, III, 457.

<sup>22</sup> *Poultry Sci.*, 1944, **23**, 525.

<sup>23</sup> O. C. Lee and R. A. Craig, *Indiana Agric. Exp. Sta.*, 1939, *Ext. Bull.* 240; B., 1945, III, 24. G. Nicol, *J. Dept. Agric. Victoria*, 1943, **41**, 255; A., 1945, III, 563. J. R. Hudson, *E. African Agric. J.*, 1944, **10**, 101; B., 1945, III, 255.

<sup>24</sup> H. M. Elder, *J. Dept. Agric. Victoria*, 1943, **41**, 173; A., 1945, III, 563. I. J. Cunningham and C. S. M. Hopkirk, *New Zealand J. Sci. Tech.*, 1945, **26**, A, 333; A., 1945, III, 790. D. G. Steyn, *S. African J. Sci.*, 1945, **41**, 243; A., 1945, III, 790.

<sup>25</sup> F. Chambers, *Vet. Rec.*, 1944, **56**, 128; A., 1945, III, 193.

<sup>26</sup> B. H. Wilford and L. O. Mott, *J. Econ. Entom.*, 1944, **37**, 291; B., 1945, III, 56.

<sup>27</sup> J. A. B. Smith and F. Baker, *Biochem. J.*, 1944, **38**, 496; A., 1945, III, 302. I. W. Rupel, G. Bohstedt, and E. B. Hart, *J. Dairy Sci.*, 1943, **26**, 647; B., 1945, III, 62.

<sup>28</sup> *J. Comp. Path. and Therap.*, 1944, **54**, 88.



for chicks and rats.<sup>29</sup> C. R. Grau and H. J. Almquist<sup>30</sup> have determined the methionine content of various protein supplements by chemical and biological procedures, and consider that this amino-acid cannot be replaced by cystine, even in the presence of high levels of choline; they found sesame protein to be deficient in lysine for chicks. D. M. Hegsted<sup>31</sup> has succeeded in growing chicks using twelve amino-acids as combined source of nitrogen, although at a slower rate than with an adequate protein.

### *Mineral Requirements and Effects.*

Most of the recent work on this subject has been in reference to effects of trace elements. Various reviews<sup>32</sup> have dealt with diseases caused by deficiencies of copper and cobalt and by excess of molybdenum. The uptake of molybdenum from the soil may be increased by liming.<sup>33</sup> "Swayback" of lambs in this country may not be due to copper deficiency in soil and herbage as previously suggested for other areas, although the lambs have copper-deficient blood; the high lead content of the soils in the area is thought to have some bearing on this anomaly.<sup>34</sup> F. Blakemore<sup>35</sup> has described the effects of fluorosis, and collaborative work on the nutritive evaluation of defluorinated phosphates has been progressing.<sup>36</sup> The maximum safe daily intake of fluorine by sheep is 1.5 to 3.0 mg. per kg. body weight.<sup>37</sup> Manganese deficiency in rabbits has a weakening effect on the bones.<sup>38</sup>

### *Vitamins and Hormones.*

C. E. Ballinger<sup>39</sup> reports that pigs that had access to good pasture from birth to 3 months did not benefit from vitamin-A supplements during the following 3 months. A New Jersey bulletin<sup>40</sup> deals with the stability of carotene in silages.

<sup>29</sup> A. A. Klose and H. L. Fevold, *J. Nutrition*, 1945, 29, 421; A., 1945, III, 673.

<sup>30</sup> *Arch. Biochem.*, 1945, 6, 287; A., 1945, III, 549. *J. Nutrition*, 1945, 29, 219; A., 1945, III, 456. *Proc. Soc. Exp. Biol. Med.*, 1944, 57, 187; A., 1945, III, 456.

<sup>31</sup> *J. Biol. Chem.*, 1944, 156, 247; A., 1945, III, 181.

<sup>32</sup> H. H. Green, *Proc. Nutrition Soc.*, 1944, 1, 177; A., 1945, III, 38. R. L. Mitchell, *ibid.*, 183; B., 1945, III, 1. T. Dalling, *ibid.*, 194; A., 1945, III, 39. C. J. Martin, *ibid.*, 195; A., 1945, III, 39. W. L. Stewart, *ibid.*, 200; A., 1945, III, 38. W. S. Ferguson, *ibid.*, 215; A., 1945, III, 39. J. D. O'Connor, *Vet. Rec.*, 1944, 56, 337; A., 1945, III, 244. J. R. Hudson, *E. African Agric. J.*, 1944, 10, 51; A., 1945, III, 870.

<sup>33</sup> N. H. Shaw, N. Barrie, and E. H. Kipps, *J. Counc. Sci. Ind. Res., Australia*, 1944, 17, 233; B., 1945, III, 88.

<sup>34</sup> G. D. Shearer and E. I. McDougall, *J. Agric. Sci.*, 1944, 34, 207; A., 1945, III, 244.

<sup>35</sup> *Proc. Nutrition Soc.*, 1944, 1, 211; A., 1945, III, 39.

<sup>36</sup> H. R. Bird, J. P. Mattingly, H. W. Titus, J. C. Hammond, W. L. Kellogg, T. B. Clark, C. E. Weakley, jun., and A. H. Van Landingham, *J. Assoc. Off. Agric. Chem.*, 1945, 28, 118; A., 1945, III, 456.

<sup>37</sup> C. L. Shrewsbury, J. D. Hatfield, L. P. Doyle, and F. N. Andrews, *Indiana Agric. Exp. Sta.*, 1944, *Bull.* 499; A., 1945, III, 871.

<sup>38</sup> S. E. Smith, M. Medlicott, and G. H. Ellis, *Arch. Biochem.*, 1944, 4, 281; A., 1945, III, 39.

<sup>39</sup> *New Zealand J. Sci. Tech.*, 1945, 26, A, 297; B., 1945, III, 173.

<sup>40</sup> J. W. Bartlett, O. F. Garrett, R. P. Reece, and R. P. Hartman, *New Jersey Agric. Exp. Sta.*, 1940, *Bull.* 675; B., 1945, III, 101.



Addition of vitamin- $B_1$  to dairy cattle rations at the rate of 300  $\mu$ g. per lb. of digestible nutrients was found to have no effect on milk production, indicating that adequate supplies of this vitamin are synthesised in the rumen.<sup>41</sup> In pigs, the  $-B_1$  contents of the diet, blood, and muscle tissue appear to be related, but that in the muscle tissue is retained after dietary  $-B_1$  is withdrawn.<sup>42</sup>

The optimum riboflavin intake of White Wyandotte chickens is 3.0 to 3.6  $\mu$ g. per g. of food.<sup>43</sup> Riboflavin deficiency in chicks appears to reduce the severity of attacks of avian malaria, but aneurin deficiency tends to increase the severity, whereas pyridoxine reduces the therapeutic value of quinine and atebirin against this disease.<sup>44</sup> The symptoms of deficiencies of pantothenic acid and of pyridoxine in pigs have been further studied,<sup>45</sup> also those of simultaneous deficiencies of pantothenic acid, biotin, and folic acid in the chick.<sup>46</sup> The pantothenic acid content of chicks remains constant during embryonic development, and is directly related to that in the diet of the hens producing the eggs.<sup>47</sup> The chick derives part of its vitamin- $B$  requirements from bacterial synthesis in the intestine, but, like the turkey, poultry, and the pig, depends also on dietary sources, *e.g.*, soya-bean meal and green leaves.<sup>48</sup> The separation and identification of other  $B$ -vitamins required by the chick (anti-anæmia and feathering factors) is progressing.<sup>49</sup> J. McGinnis, L. C. Norris, and G. F. Heuser<sup>50</sup> have continued their investigation of the antiperotic properties of betaine, methionine, and choline.

N. J. Scorgie and W. C. Miller<sup>51</sup> have further studied the alleged toxicity of various liver oils when fed in excess to pigs. They confirmed that growth retardation occurs owing to mechanical laxative effects, but

<sup>41</sup> J. K. Loosli and H. L. Lucas, *J. Dairy Sci.*, 1943, **26**, 291; B., 1945, III, 42.

<sup>42</sup> J. W. Pence, R. C. Miller, R. A. Dutcher, and W. T. S. Thorp, *J. Biol. Chem.*, 1945, **158**, 647; A., 1945, III, 775. J. W. Pence, R. C. Miller, R. A. Dutcher, and P. T. Ziegler, *J. Animal Sci.*, 1945, **4**, 141; A., 1946, III, 469.

<sup>43</sup> W. Bolton, *J. Agric. Sci.*, 1944, **34**, 198; A., 1945, III, 245.

<sup>44</sup> M. M. Brooke, *Amer. J. Hyg.*, 1945, **41**, 81; A., 1945, III, 376. A. O. Seeler and W. H. Ott, *J. Infect. Dis.*, 1944, **75**, 175; A., 1945, III, 245. A. O. Seeler, *Proc. Soc. Exp. Biol. Med.*, 1944, **57**, 113; A., 1945, III, 311.

<sup>45</sup> R. H. Follis, jun., and M. M. Wintrobe, *J. Exp. Med.*, 1945, **81**, 539; A., 1945, III, 776. G. E. Cartwright, M. M. Wintrobe, P. Jones, M. Lauritsen, and S. Humphreys, *Johns Hopkins Hosp. Bull.*, 1944, **75**, 35; A., 1945, III, 247.

<sup>46</sup> J. H. Shaw and P. H. Phillips, *J. Nutrition*, 1945, **29**, 107; A., 1945, III, 460.

<sup>47</sup> P. B. Pearson, V. H. Melass, and R. M. Sherwood, *Arch. Biochem.*, 1945, **7**, 353; A., 1945, III, 873.

<sup>48</sup> C. J. Campbell, R. A. Brown, and A. D. Emmett, *J. Biol. Chem.*, 1944, **154**, 721; A., 1945, III, 42. B. L. O'Dell, *Univ. Microfilms Ann Arbor*, 1944, **5**, No. 2, 19; A., 1945, III, 777. P. R. Burkholder, I. McVeigh, and K. Wilson, *Arch. Biochem.*, 1945, **7**, 287; A., 1945, III, 894. L. R. Richardson, A. G. Hogan, and H. L. Kempster, *J. Nutrition*, 1945, **30**, 151; A., 1945, III, 873. H. Heitman, jun., *Univ. Microfilms Ann Arbor*, 1944, **5**, No. 2, 14; A., 1945, III, 773.

<sup>49</sup> F. W. Hill, L. C. Norris, and G. F. Heuser, *J. Nutrition*, 1944, **28**, 175; A., 1945, III, 40. G. M. Briggs, jun., T. D. Luckey, C. A. Elvehjem, and E. B. Hart, *J. Biol. Chem.*, 1945, **158**, 303; A., 1945, III, 553. M. L. Scott, L. C. Norris, G. F. Heuser, and W. F. Bruce, *ibid.*, 291; A., 1945, III, 553.

<sup>50</sup> *Proc. Soc. Exp. Biol. Med.*, 1944, **56**, 197; A., 1945, III, 181.

<sup>51</sup> *Empire J. Exp. Agric.*, 1944, **12**, No. 46, 74.



obtained no evidence of degenerative changes in skeletal muscles described by continental workers and ascribed to destruction of vitamin-*E*. E. W. McChesney<sup>52</sup> has found that there are essential differences between the metabolism of vitamins-*D*<sub>2</sub> and -*D*<sub>3</sub> by the chick; A. Krupski<sup>53</sup> has described a condition of osteoporosis in calves not due to vitamin-*D* deficiency.

Hormonal control of lactation in cattle, and of fattening of poultry, has not yet reached the stage of practical application, but appears to be approaching thereto.<sup>54</sup>

### *Evaluation and Preservation of Crops.*

A joint committee of the American Society of Agronomy, the American Dairy Science Association, and the American Society of Animal Production has issued a lengthy preliminary report<sup>55</sup> on pasture investigations technique, aiming at making such investigations of more value both locally and universally. W. D. Andrew and others<sup>56</sup> have found that in Victoria, Australia, phosphorus deficiency in the soil is a major agricultural problem. Studies regarding seasonal variations of chemical composition of pastures have been made in Canada<sup>57</sup> and New Mexico,<sup>58</sup> and regarding the suitability of various grasses and clovers for temporary leys in East Africa<sup>59</sup> and U.S.A.<sup>60</sup> W. B. Nevens<sup>61</sup> stresses the ability to suppress weeds as an important criterion of suitability for forage crops.

A bulletin from New Jersey<sup>62</sup> gives the composition of 100 samples of grasses and legumes and of their corresponding silages, prepared with phosphoric acid or molasses; a loss of 10—15% of the original dry matter is unavoidable, but the essential nutrients can be retained by suitable control. With a cereal-legume crop, maximum protein content in the silage is attained by cutting at the flower-emergence stage.<sup>63</sup> Another bulletin, from Pennsylvania,<sup>64</sup> deals with the effects of various factors,

<sup>52</sup> *Proc. Soc. Exp. Biol. Med.*, 1945, **58**, 300; A., 1945, III, 779.

<sup>53</sup> *Z. Vitaminforsch.*, 1944, **14**, 300; A., 1945, III, 772.

<sup>54</sup> S. J. Folley, *J. Soc. Arts*, 1945, **93**, 114; B., 1945, III, 76. R. G. Jaap and R. B. Thompson, *U.S. Egg and Poultry Mag.*, 1945, **15**, 108; B., 1945, III, 148.

<sup>55</sup> *J. Dairy Sci.*, 1943, **26**, 353; B., 1945, III, 35.

<sup>56</sup> W. D. Andrew, *J. Dept. Agric. Victoria*, 1942, **40**, 385, 430. *Ibid.*, 1944, **42**, 241, 274; B., 1945, III, 217. *Ibid.*, 1943, **41**, 277; B., 1945, III, 157. A. Morgan, *ibid.*, 349; B., 1945, III, 217. G. B. Rayner, *ibid.*, 353; B., 1945, III, 217. L. C. Bartels, *ibid.*, 1944, **42**, 481; B., 1945, III, 219.

<sup>57</sup> E. W. Crampton and I. R. C. Jackson, *J. Animal Sci.*, 1944, **3**, 333.

<sup>58</sup> W. E. Watkins and J. H. Knox, *ibid.*, 1945, **4**, 297.

<sup>59</sup> D. C. Edwards, *E. African Agric. J.*, 1943, **9**, 62; B., 1945, III, 254.

<sup>60</sup> M. E. Ensminger, H. G. McDonald, A. G. Law, E. J. Warwick, E. J. Kreitzinger, and V. B. Hawk, *Wash. Agric. Exp. Sta.*, 1944, *Bull.* 444; B., 1945, III, 107. R. W. Kidder, *J. Agric. Res.*, 1945, **70**, 89; B., 1945, III, 147.

<sup>61</sup> *J. Dairy Sci.*, 1943, **26**, 877; B., 1945, III, 107.

<sup>62</sup> M. W. Taylor, C. B. Bender, and W. C. Russell, *New Jersey Agric. Exp. Sta.*, 1940, *Bull.* 683; B., 1945, III, 106.

<sup>63</sup> H. I. Moore and J. S. Willcox, *J. Min. Agric.*, 1945, **51**, 502; B., 1945, III, 106.

<sup>64</sup> R. W. Stone, S. I. Bechdel, H. D. McAuliffe, F. R. Murdock, and R. C. Malzahn, *Pennsylvania Agric. Exp. Sta.*, 1943, *Bull.* 444; B., 1945, III, 78.



*e.g.*, phosphoric acid, salt, molasses, wilting, and inoculum, on the bacterial flora of lucerne silage; salt helps to express the plant juice, and thus to promote tight packing, whilst wilting is useful when it is necessary to increase the fermentable sugar content of the crop. Wastage due to localised spoilage is liable to occur in concrete silos around the joints, unless these are pointed with cement; artificial heating of the crop as it is filled into the silo saves delay in dealing with early crops.<sup>65</sup> Neutralisation of phosphoric acid oat silage with limestone and sodium bicarbonate is sometimes useful in increasing palatability.<sup>66</sup> Atlas sorgo silage has been found to be comparable with that prepared from maize.<sup>67</sup>

Bulletins from Virginia, Ohio, and Missouri<sup>68</sup> deal with the nutritive values of various hays; change from one hay to another is suggested as one means of overcoming shortcomings. J. B. Firth and R. E. Stuckey<sup>69</sup> have discussed methods of examining burnt hay ricks in order to determine whether combustion was spontaneous or otherwise.

Various aspects of grass drying were discussed at a joint meeting of agriculturalists and chemical engineers,<sup>70</sup> and the superiority of the product, from the nutritional viewpoint, over that produced by sun-curing was demonstrated. Further evidence of the nutritional value of artificially dehydrated hays and vegetable wastes is available from America and New Zealand.<sup>71</sup>

One of the problems arising from the storage of feeds which has not yet been solved is that of carotene loss.<sup>cf.21,22</sup> In compound feeds, fatty acid peroxides introduced by ingredients such as meat and fish meals are apparently responsible for the carotene loss.<sup>72</sup> R. C. Mills and E. B. Hart<sup>73</sup> have experimented with various chemical treatments to reduce this loss, without much success; they found that autoclaving at 15 lb. pressure for one hour destroyed carotene oxidase and chlorophyll, but that even this did not prevent loss of carotene unless access of oxygen was prevented. The retention of members of the vitamin-B complex

<sup>65</sup> A. Amos, *J. Min. Agric.*, 1945, **52**, 151, 152; B., 1945, III, 254.

<sup>66</sup> W. A. King, *J. Dairy Sci.*, 1943, **26**, 975; B., 1945, III, 107.

<sup>67</sup> F. G. King, *Indiana Agric. Exp. Sta.*, 1944, *Bull.* 500; B., 1945, III, 255.

<sup>68</sup> C. W. Holdaway, W. B. Ellett, J. F. Eheart, and A. D. Pratt, *Virginia Agric. Exp. Sta.*, 1939, *Tech. Bull.* 65; B., 1945, III, 107. C. C. Hayden, *Ohio Agric. Exp. Sta.*, 1942, *Bull.* 631; B., 1945, III, 173. E. W. Swanson and H. A. Herman, *Missouri Agric. Exp. Sta.*, 1943, *Res. Bull.* 372; B., 1945, III, 192.

<sup>69</sup> *J.S.C.I.*, 1945, **64**, 13; B., 1945, III, 69.

<sup>70</sup> S. J. Watson, A. Goldberg, A. C. Bartelli, and D. Fairclough, *Chem. Eng. Group, Inst. Chem. Eng., and Agric. Group, Soc. Chem. Ind.*, Nov., 1944, *Preprints*; B., 1945, III, 23.

<sup>71</sup> S. I. Bechdel, A. W. Clyde, C. O. Cromer, and P. S. Williams, *Pennsylvania Agric. Exp. Sta.*, 1940, *Bull.* 396; B., 1945, III, 232. A. E. Tomhave, E. Hoffmann, E. G. Kelley, M. E. Wall, and D. A. Colker, *Delaware Agric. Exp. Sta.*, 1944, *Bull.* 247. D. A. Colker and R. K. Eskew, *Fruit Prod. J.*, 1945, **24**, 302, 317; B., 1945, III, 230. F. D. Collins and F. B. Shorland, *New Zealand J. Sci. Tech.*, 1945, **26**, A, 372; B., 1945, III, 210.

<sup>72</sup> G. S. Fraps, W. W. Meinke, R. Reiser, and R. M. Sherwood, *Texas Agric. Exp. Sta.*, 1943, *Bull.* 637; B., 1945, III, 107.

<sup>73</sup> *J. Dairy Sci.*, 1945, **28**, 1, 339.



does not present such a problem.<sup>74</sup> Mould spoilage on storage can be controlled by maintaining the relative humidity below 75%.<sup>75</sup>

### *Processed Feeding Stuffs and Waste Products.*

Various exploratory investigations have been made with the object of extending the range of natural products used as feeding stuffs. Ripe elderberries gave promising results, but not horse chestnuts.<sup>76</sup> The digestibility of bracken and bracken ensilage is low, presumably owing to the high lignin content even in the young stage.<sup>77</sup> Pea pods give an excellent silage for ruminants, but are of little value for pig-feeding.<sup>78</sup> Rye grass seed is comparable with oats.<sup>79</sup> In East Africa, pumpkins, baobab fruit, and Karoo have been found to have some value.<sup>80</sup> In Texas, a ration containing 50% of the total concentrates as dried citrus peel and pulp gave satisfactory milk production.<sup>81</sup> The various varieties of cottonseed are not equally deleterious to cattle.<sup>82</sup>

D. Snow, J. A. B. Smith, and N. C. Wright<sup>83</sup> have recommended methods of incorporating urea and other non-protein nitrogen compounds in feeding stuffs and preventing loss of nitrogen on storage. A predigestion process for improving the digestibility of fibrous materials by cattle has been patented.<sup>84</sup>

### FRUIT AND VEGETABLES.

By far the greater part of the work published has been concerned with the nutritive qualities of fruit and vegetables, particularly the vitamin contents, on which knowledge has been extended very considerably as a result of the examination of products indigenous to various countries, of a range of varieties of certain fruits, etc. Considerable attention has been paid to guavas. For example, C. D. Miller<sup>85</sup> has found that those grown in Hawaii are five times as rich in ascorbic acid as orange juice; D. P. Van der Merwe,<sup>86</sup> studying the variations in vitamin content of this fruit, obtained values ranging from 100 mg. to 700 mg. per 100 g. and found a tendency for the content to increase throughout the season.

<sup>74</sup> C. C. Lardinois, C. A. Elvehjem, and E. B. Hart, *J. Dairy Sci.*, 1944, **27**, 875.

<sup>75</sup> D. Snow, M. H. G. Crichton, and N. C. Wright, *Ann. Appl. Biol.*, 1944, **31**, 102; B., 1945, III, 23.

<sup>76</sup> H. Templeton, *Nature*, 1943, **152**, 345; B., 1945, III, 23.

<sup>77</sup> W. S. Ferguson and E. R. Armitage, *J. Agric. Sci.*, 1944, **34**, 165; B., 1945, III, 24. W. S. Ferguson and O. Neave, *ibid.*, 172; B., 1945, III, 24.

<sup>78</sup> H. E. Woodman and R. E. Evans, *ibid.*, 155; B., 1945, III, 24.

<sup>79</sup> R. H. Common, *ibid.*, 1945, **35**, 56; B., 1945, III, 107.

<sup>80</sup> M. H. French, *E. African Agric. J.*, 1944, **9**, 221; B., 1945, III, 255. *Ibid.*, 144; B., 1945, III, 255. M. Henrici, *S. African J. Sci.*, 1945, **41**, 213; B., 1945, III, 256.

<sup>81</sup> O. C. Copeland and C. N. Shepardson, *Texas Agric. Exp. Sta.*, 1944, *Bull.* 658; B., 1945, III, 173.

<sup>82</sup> L. C. Dharmani, *Indian Farming*, 1944, **5**, 459; B., 1945, III, 148.

<sup>83</sup> *J. Agric. Sci.*, 1945, **25**, 65; B., 1945, III, 173.

<sup>84</sup> E. A. Ritter and C. Lipschitz, B.P. 567,857; B., 1945, III, 130.

<sup>85</sup> *Proc. Pacific Sci. Congr., Pacific Sci. Assoc.*, 1943, **6**, 403.

<sup>86</sup> *Clin. Proc. (Cape Town, S.A.)*, 1944, **3**, 441.



This fruit has been studied by W. V. Cruess and his co-workers<sup>87</sup> with particular reference to the products (jams, jellies, and dehydrated, canned, or frozen products) that might be prepared in order to utilise the high ascorbic acid content (55—480 mg. per 100 g.) of the American-grown fruits to the best advantage. Guavas were also included in a range of tropical and semi-tropical fruits including papaya, mangoes, pineapple, orange, and grapefruit examined by V. L. Quinones, N. B. Guerrant, and R. A. Dutcher.<sup>88</sup> The authors determined ascorbic acid, carotene, thiamin, and riboflavin on each and confirmed the value of guavas as a source of ascorbic acid, finding papaya also a valuable source of this vitamin as well as of carotene.

Work on the variations in vitamin content and composition during growth has been carried out by P. L. Harding and D. F. Fisher<sup>89</sup> on two varieties of Florida grapefruit. The authors report detailed analyses for the ascorbic acid, mineral, pectin, and sugar contents, and show that the ascorbic acid content tends to fall as the fruit ripens, but is correlated with the juice content; iron, potassium, calcium, magnesium, and manganese contents were also given. Soluble and middle lamella pectin were greatest in the immature fruit, decreasing as the fruit ripened; the sugars increased and the acidity fell during ripening, as is to be expected.

A study of 13 varieties of apples grown in W. Virginia has been made by V. B. Fish, R. B. Dustman, and R. S. Marsh<sup>90</sup>; it was found that the varieties fell into three classes, those having ascorbic acid contents of 15—20 mg. per 100 g. (Duchess being a typical example), those having contents of 10—15 mg. (Jonathan and Winesap), and those between 7 and 10 mg. (McIntosh). Harvesting two weeks before maturity, for ripening in store, led to a loss of ascorbic acid, whilst allowing the fruit to remain on the tree after maturity led to a slight increase.

The distribution of ascorbic acid in the potato plant during growth and in the tubers on harvesting has been investigated by L. H. Lampitt, L. C. Baker, and T. L. Parkinson.<sup>91</sup> The vitamin was found chiefly in the leaves and new tubers and the concentration became constant after about three months' growth, the total increasing in proportion to the growth of the plant. Regarding the distribution in the tubers, the authors found little difference between the concentration in the peel and that in the remainder of the tissue unless sprouting had occurred, when a concentration occurred in the sprouts and eyes. After harvesting, the ascorbic acid content of potatoes was found to fall steadily from August to January and then to remain fairly constant at about 25% of its initial value, these changes being independent of variety. The

<sup>87</sup> W. V. Cruess, L. A. Hohl, M. A. Jimenez, S. Nichols-Roy, R. Torres, and M. Zorilla, *Fruit Prod. J.*, 1945, **24**, 263, 283, 285; B., 1945, III, 172.

<sup>88</sup> *Food Res.*, 1944, **9**, 415; A., 1945, III, 115.

<sup>89</sup> U.S. Dept. Agric., 1945, *Tech. Bull.* 886; cf. A., 1945, III, 704.

<sup>90</sup> *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 196; B., 1945, III, 21.

<sup>91</sup> *J.S.C.I.*, 1945, **64**, 18, 22; B., 1945, III, 77.



same authors<sup>92</sup> have also studied the changes in ascorbic acid content occurring after harvesting in a wide range of vegetables and find that at room temperature a fairly rapid loss occurs at different rates for different vegetables; storage at 3° c. materially reduced the rate of loss, and in fact, in certain cases (notably lettuce, broccoli, and cabbage), an increase occurred in the first few days. A useful table summarising 850 results of the determination of ascorbic acid in raw vegetables is given.

Work of interest from a fundamental viewpoint has been published on the ascorbic acid content of tomatoes grown in sand culture and the effect of mineral ions.<sup>93</sup> Calcium and nitrate exerted marked effects on growth and fruitfulness, while a higher ascorbic acid content resulted from sulphate deficiency; it was subnormal when potassium or phosphate was deficient. The work has been continued<sup>94</sup> by a study of the effects of environment factors (such as light intensity, temperature, etc.). An increase of 66% in the ascorbic acid content was found when the plants were transferred from shade to sunlight when the fruits were grown but green. Slight decreases were found to result from a reduction in the temperature or by the application of nitrogen but the light factor was by far the most important.

The possible uses of germinated peas, soya beans, etc. as sources of vitamins (first developed in 1919 by H. Chick and E. M. Delf<sup>95</sup>) have been investigated in considerable detail by C. E. French and his co-workers.<sup>96</sup> Dried peas gave the best results and after germinating treatment for 72 hours the 2-inch sprouts produced contained 25 mg. of ascorbic acid per 100 g., and were fair sources of riboflavin and nicotinic acid but poor sources of thiamin. Soya beans were also of value although inferior to peas.

The use of ascorbic acid for the prevention of browning of cut apples<sup>97</sup> and peaches<sup>98</sup> in place of the normal agents, such as sulphur dioxide and thiourea etc., has received some investigation. While satisfactory methods of treatment can be devised and the procedure is desirable from a dietetic point of view, the cost at present is prohibitive. In the course of the work it was noted that the portions of fruit not covered by liquid tended to brown readily and it would appear from the work of H. Deuel,<sup>99</sup> which showed that in the presence of air or oxygen ascorbic acid acted as an oxygen carrier and could cause oxidative degradation of pectin, that in certain conditions ascorbic acid might be expected to accentuate

<sup>92</sup> *J.S.C.I.*, 1945, **64**, 200, 202; *B.*, 1945, **III**, 208.

<sup>93</sup> K. C. Hamner, C. B. Lyon, and C. L. Hamner, *Bot. Gaz.*, 1942, **103**, 586; *A.*, 1945, **III**, 70.

<sup>94</sup> K. C. Hamner, L. Bernstein, and L. A. Maynard, *J. Nutrition*, 1945, **29**, 85; *B.*, 1945, **III**, 147.

<sup>95</sup> *Biochem. J.*, 1919, **13**, 199.

<sup>96</sup> C. E. French, G. H. Berryman, J. T. Goorley, H. A. Harper, D. M. Harkness, and E. J. Thacker, *J. Nutrition*, 1944, **28**, 63; *A.*, 1944, **III**, 751.

<sup>97</sup> M. MacArthur, *Canad. Food Packer*, 1945, **16**, No. 8, 13.

<sup>98</sup> J. C. Bauernfeind and G. F. Siemers, *Quick Frozen Foods*, 1945, **7**, No. 12, 46, 60.

<sup>99</sup> *Mitt. Lebensm. Hyg.*, 1943, **34**, 333; *A.*, 1946, **II**, 371.



browning. What may be a related phenomenon has been reported by S. M. Prokoshev,<sup>100</sup> who found that when potatoes were sliced and exposed to air or oxygen the ascorbic acid increased from 10.8 mg. per 100 g. to 24.1 mg., no increase occurring in the absence of oxygen.

### *Dehydration.*

Much work has been carried out on the methods of preparing fruit and vegetables prior to drying, particularly on the advantages of sulphiting. Thus, G. Mackinney<sup>101</sup> found that sulphiting was desirable on the grounds that a more uniformly dried product is obtained, scorching is avoided, and a lower moisture content attainable giving improved keeping qualities; the desirable residual sulphur dioxide content was stated to be 200—500 p.p.m. Similar advantages were noted by C. J. Tressler<sup>102</sup> on the sulphiting of potatoes before drying, while Cruess and his co-workers<sup>103</sup> recommend for fruit to be shipped and stored under tropical conditions a very high sulphur dioxide content (about 14,000 p.p.m.) obtained by dry sulphuring the partly dried fruit. The use of sulphur dioxide in place of blanching for the inactivation of peroxidase and catalase in carrots, potatoes, spinach, etc. has been investigated by H. D. Brown, R. M. Short, and E. K. Alban<sup>104</sup>; these workers found that while inactivation could be attained, the sulphite-treated vegetables did not give dehydrated products as satisfactory as did those blanched by steam, although somewhat better ascorbic acid retention was obtained.

The relative merits of 19 American varieties of potatoes for dehydration have been considered by J. S. Caldwell, C. W. Culpepper, and P. M. Lombard.<sup>105</sup> It was concluded that there was no one variety to be recommended in preference to the others, nor was the quality of the dehydrated product correlated with the locality of growth. A correlation was, however, found between the suitability for drying and the rate of application of an 8 : 16 : 14 N-P-K fertiliser; a rate of application greater than 1000 lb. per acre gave markedly poorer quality. J. S. Caldwell, C. W. Culpepper, and F. J. Stevenson<sup>106</sup> have examined the relation between the degree of maturity of the potatoes and the quality of the dehydrated product with the conclusion that immature potatoes were very undesirable for drying.

### *Cool Storage.*

Little work has been published and what there is is concerned with the effects of various fumigation and spray treatments rather than with fundamental aspects of the subject. For example, it has been shown

<sup>100</sup> *Biochimia*, 1944, **9**, 36; A., 1945, III, 184.

<sup>101</sup> *Fruit Prod. J.*, 1945, **24**, 300; B., 1945, III, 230.

<sup>102</sup> *Ibid.*, 104; B., 1945, III, 103.

<sup>103</sup> W. V. Cruess, H. Friar, E. G. Balog, and P. van Holten, *ibid.*, 103, 121; B., 1945, III, 104.

<sup>104</sup> *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 193; B., 1945, III, 21.

<sup>105</sup> *Amer. Potato J.*, 1944, **21**, 211.

<sup>106</sup> *Ibid.*, 217.



that the absorption of hydrocyanic acid by oranges was doubled when the fruits were treated under vacuum (26 in.) instead of at atmospheric pressure, and that the injury to the fruits was greater.<sup>107</sup> The spoilage of oranges from stem-end rot and green mould decay during storage can be prevented by the application of a 5% aqueous solution of thiourea; this treatment was found to be effective even after ethylene treatment.<sup>108</sup>

### *Preservation.*

A detailed study of the preservation by salting of a wide range of vegetables (beets, carrots, corn, beans, spinach, etc.) has been made by F. W. Fabian and C. K. Wadsworth.<sup>109</sup> In all cases better results were obtained by salting the blanched vegetables in a strong brine (18%) rather than in a weak one (3%), and no advantage was found in the addition of acetic acid to the stronger brine. Vegetables preserved by salting would appear to be poor sources of ascorbic acid, as the losses were great (of the order of 100%); on the other hand, carotene losses were small.

The factors affecting the quality of canned orange juice, with particular reference to exposure to oxygen, volatile oil content, and heat-treatment, have been investigated by J. M. Boyd and G. T. Peterson.<sup>110</sup> While avoidance of contact with oxygen was desirable, for which purpose the use of an atmosphere of nitrogen was recommended in preference to carbon dioxide, the major cause of deterioration was the heat-treatment. The procedure recommended by the authors was the extraction and canning of the juice in an atmosphere of nitrogen under aseptic conditions from fruit which had received a surface sterilisation treatment (by steam or antiseptics), the avoidance of expression of oil from the peel being important. The recommended heat-treatment after canning was the raising of the temperature to 240° F. in 2 seconds and immediate cooling to 100° F. The advisability of cool storage conditions for the canned juice is stressed.

### *Miscellaneous.*

Knowledge regarding plant hormones has been increased by the findings of F. W. Allen and A. E. Davey<sup>111</sup> that the spraying of Bartlett pear trees to increase the proportion of fruit setting led to a greater loss after harvesting, owing to an accelerated rate of ripening. Fruit from trees so treated must therefore be placed in cool storage as rapidly as possible. Similarly, J. W. Mitchell and P. C. Marth<sup>112</sup> found that the application of 2:4-dichlorophenoxyacetic acid materially shortened the time required for ripening bananas, apples, and pears after harvesting; on the other

<sup>107</sup> E. T. Bartholomew, W. B. Sinclair, and D. L. Lindgren, *Plant Physiol.*, 1945, 20, 62; B., 1945, III, 160.

<sup>108</sup> J. F. L. Childs and E. A. Siegler, *Phytopath.*, 1944, 34, 983.

<sup>109</sup> *Fruit Prod. J.*, 1945, 24, 231, 247; B., 1945, III, 170.

<sup>110</sup> *Ind. Eng. Chem.*, 1945, 37, 370; B., 1945, III, 208.

<sup>111</sup> *Blue Anchor*, 1945, 22, No. 1, 9, 25, 30.

<sup>112</sup> *Bot. Gaz.*, 1944, 106, 199.



hand, such an application was without effect on tomatoes, persimmons, and peppers.

The principles of chromatographic analysis have been applied to the study of fruit and vegetable extracts both from a fundamental point of view and for the purposes of routine analysis; thus, S. Lassen, K. Bacon, and J. Sutherland,<sup>113</sup> by absorption of extracts on magnesia, have demonstrated the presence of  $\alpha$ - and  $\beta$ -carotenes in avocado pears together with a carotene of unknown spectrophotometric transmission characteristics, whilst W. Mischon<sup>114</sup> has used absorption on alumina as a means of separating artificial from natural colouring matters in fruit juices and drinks.

In the course of a study on the raising of varieties of potatoes which are immune from darkening after cooking, H. Schmalfuss, G. Stelzner, and W. Kröner<sup>115</sup> have developed a test to indicate the liability to darken which consists of comparing the colour of the cooked potato when mashed with and without the addition of ferric chloride solution; the ferric ion serves to enhance the normal darkening effect and the sensitivity towards iron is an indication of the liability to darken.

A method for the preparation of pectic material of reduced methoxyl content from the wastes of citrus fruit and of apples has been described by H. S. Owens, R. M. McCready, and W. D. Maclay,<sup>116</sup> the procedure being to raise the pH of the material to about 9, at which value the esterase naturally present has its maximum activity; after the required degree of de-esterification has been reached, the enzyme is destroyed by acidification and heating at 70° c. for 15 minutes. The modified pectins are then extracted with a solution of Calgon and precipitated or concentrated as in the normal procedure for pectin manufacture.

## CEREALS AND CEREAL FOODS.

### *Dough as an Oxidation-Reduction System.*

The softening that takes place in dough on keeping is ascribed by E. Elion<sup>117</sup> to the action of proteolytic enzymes, activated by reducing substances (e.g., glutathione) present in the dough; oxidising agents owe their so-called "improving" action (a) to the immediate elimination of the reducing substances of the flour and (b) to a slower, direct effect on the enzymes. In addition to oxidising agents, ascorbic acid has been found effective as a bread "improver." An ascorbic acid oxidase has been shown to be present in flour and it is inferred—and there is some experimental evidence in support—that ascorbic acid is converted by this enzyme into dehydroascorbic acid, which acts as the improving

<sup>113</sup> *Food Res.*, 1944, **9**, 427; A., 1945, III, 336.

<sup>114</sup> *Deut. Lebensm.-Rundschau*, 1943, 49.

<sup>115</sup> *Z. Spiritusind.*, 1943, **66**, No. 22/25, 1.

<sup>116</sup> *Ind. Eng. Chem.*, 1944, **36**, 936; B., 1945, III, 41.

<sup>117</sup> *Bakers' Digest*, 1945, **19**, 31, 43; B., 1945, III, 187.



agent either by oxidising the thiol-containing substances in the flour or by inactivating the proteolytic enzymes.<sup>118,119</sup>

E. Elion<sup>120</sup> states that organic compounds containing the  $\cdot\text{C}(\text{OH})\text{:C}(\text{OH})\cdot\text{CO}\cdot$  group (*e.g.*, reductone, reductic acid) act in a similar manner to bromate and to ascorbic acid as "improvers" in bread dough. R. M. Sandstedt and B. D. Hites,<sup>119</sup> however, found reductone to be ineffective as an "improver."

### Vitamins.

It is essential that the necessary storage and processing of the raw materials for foods should cause the least possible loss of the vitamins present in the natural product. As aneurin is unstable to heat in an alkaline medium serious loss may occur in the baking of certain types of biscuit in which alkaline residues from baking powder are present. In cereal breakfast foods the loss of aneurin is negligible when the time of cooking is short (*e.g.*, 15 minutes) but may be considerable for foods requiring prolonged cooking or in which the pH is high.<sup>121</sup> Loss of aneurin on storage of breakfast foods is slight.<sup>122</sup> In Zwieback (a type of breakfast rusk) there is an 18% loss of aneurin in baking and a further 20% loss during the subsequent toasting.<sup>123</sup>

### Analytical.

Results of comprehensive analyses of wheat, and rye and of flours of various extractions produced from them, together with calorific values, are given by R. A. McCance *et al.*<sup>124</sup> The protein, fat, fibre, aneurin, riboflavin, nicotinic acid, sodium, potassium, calcium, magnesium, iron, copper, zinc, and phosphorus contents of flour increase directly with the degree of extraction. Carbohydrate content and calorific value fall as the degree of extraction of the flour increases. This is of especial value taken in conjunction with the newer knowledge of the distribution of the vitamins in the various parts of the wheat grain.

Boron would appear to be more evenly distributed throughout the grain than many other trace elements, as bread made from 70, 85, and 100% extraction flour was found by G. Bertrand and L. Silberstein<sup>125</sup> to contain 5.7, 6.3, and 6.6 mg. of boron per kg.

The wheat grain contains a diversity of enzymes to control its metabolism; the importance of these enzymes in the process of breadmaking is becoming more fully appreciated. R. G. Booth<sup>126</sup> has applied two

<sup>118</sup> J. Melville and H. T. Shattock, *Cereal Chem.*, 1938, **15**, 201.

<sup>119</sup> R. M. Sandstedt and B. D. Hites, *ibid.*, 1945, **22**, 161; B., 1945, III, 250.

<sup>120</sup> *Ibid.*, 1944, **21**, 314; B., 1945, III, 17.

<sup>121</sup> H. Lincoln, E. L. Hove, and C. G. Harrel, *ibid.*, 274; B., 1945, III, 17.

<sup>122</sup> A. D. Robinson, M. C. Hiltz, R. Campbell, and A. Levinson, *Canad. J. Res.*, 1945, **23**, F, 1; B., 1945, III, 145.

<sup>123</sup> R. B. Meckel and G. Anderson, *Cereal Chem.*, 1944, **21**, 280; B., 1945, III, 17.

<sup>124</sup> R. A. McCance, E. M. Widdowson, T. Moran, W. J. S. Pringle, and T. F. Macrao, *Biochem. J.*, 1945, **39**, 213; B., 1945, III, 248.

<sup>125</sup> *Compt. rend.*, 1944, **218**, 532; B., 1945, III, 249.

<sup>126</sup> R. G. Booth, *Biochem. J.*, 1944, **38**, 355; C., 1945, 116.



known methods, depending on the freeing (and subsequent colorimetric determination) of phenol from sodium phenyl phosphate, to the determination of the phosphatase activity of wheat. The determination of phosphatase activity has since been used as an indicator of damage to wheat caused by overheating during the process of drying on the farm: such overheating causes a reduction in phosphatase activity and a parallel loss in vitality of the grain and in the bread-making properties of the flour made from it.

#### *Insecticides.*

The "inert dust" type of insecticide, which is believed to act by disrupting the water-retention control mechanism of the insect and so causing its desiccation and final death, includes finely ground materials from many sources. Burnt, powdered paddy-husk is recommended by M. J. Narasimhan and B. K. Murthy<sup>127</sup> for the control of insects infesting rice and other cereals. J. S. Fitzgerald<sup>128</sup> has examined numerous mineral dusts, of which the most effective were coke, calcined diatomaceous earth, dolomite, limestone, copper oxide, limonite, magnesite, rock phosphate, silica, and anhydrite.

#### *Physical Testing by Mechanical Means.*

Numerous machines have been developed and have been widely used for some years for determining the physical properties of flour doughs. In most cases they do no more than record some composite value that may include the properties of viscosity, plasticity, extensibility, elasticity, etc. Their value is in providing a rapid and reproducible picture of the general physical character of the dough, and much effort has been directed towards the correlation of this picture with the baking properties of the flour.

The Farinograph and the Mixograph consist of small mixing machines, motor-driven, coupled to a mechanical device for measuring and recording the work done during the mixing of flour and water to form a dough. As mixing proceeds, the mechanical resistance of the dough increases to a maximum and then falls. The Alveograph and the Extensograph are used to determine the extensibility and resistance to extension of flour doughs. From the graphical records of dough properties given by these machines it is possible to deduce the probable bread-making properties of the flour in so far as these are affected by the physical properties of the dough. Investigational work on the physical methods of flour testing falls under two headings: (1) work designed to improve the reproducibility of the tests and concerned with the effect of varying conditions, *e.g.*, time and temperature of mixing, proportion of water to flour, addition of yeast, salt, and chemical substances, and (2) work concerned with the correlation of the results of physical tests with information on flour quality obtained by other means. R. H. Harris, L. D.

<sup>127</sup> *Current Sci.*, 1944, **13**, 162; *B.*, 1945, **III**, 17.

<sup>128</sup> *Counc. Sci. Ind. Res. Australia*, 1944, *Bull.* 182; *B.*, 1945, **III**, 75.



Sibbit, and G. M. Scott<sup>129</sup> stress the importance of accurate temperature control in the use of the Mixograph, showing the effect of different temperatures on the shape, height, and width of the curves. T. R. Aitken, M. H. Fisher, and J. A. Anderson<sup>130</sup> have examined the reproducibility of the curves obtained with the Extensograph and the Alveograph. They suggest that all Extensograph results may be put on a comparable basis, despite the effect of adjusting the machine to different "sensitivity," by expressing all results as grams of resistance to extension. They find also that the method of dough extrusion employed to give the quintuplicate samples used for Alveograph tests gives rise to a regular variation in results of such samples indicating some changes in dough properties as the extrusion proceeds. The same authors<sup>131</sup> correlated the results of Farinograph, Extensograph, and Alveograph tests with loaf volume and protein content. They found that for Canadian wheats each method of test grouped the various wheats similarly. Taking loaf volume as a criterion of the baking quality of the flour, the physical methods of testing, used alone, were not superior to determination of protein content as a method of gauging flour quality but, by combining the results of the determination of protein content and height of Alveograph curve, a significantly higher correlation coefficient with loaf volume was obtained than when protein content alone was employed.

Comparison of the area under the curves given by the Mixograph with various soft wheat flours has shown this value to correlate well with viscosity of flour suspension, loaf volume, and "cookie spread."<sup>132</sup> C. A. Lamb<sup>133</sup> extended the Mixograph test to compare wheat samples by adopting a standard technique of tempering, grinding, and sifting the wheat. He found good correlation between the results of viscosity tests and the Mixograph curve-areas of the ground wheat and of flour produced from the wheat.

By the use of the Mixograph, C. O. Swanson and A. C. Andrews<sup>134</sup> compared the effect of adding papain, yeast-water, cysteine, and glutathione to a flour dough. All gave a similar softening and weakening effect to the flour dough but papain caused also a loss in the amount of gluten recoverable from the dough. The results were interpreted to mean that whereas all these agents cause a softening of the dough, only papain causes an enzymic disintegration of the gluten.

The Amylograph is a type of viscometer specially adapted for measuring the effect of enzymes in modifying the viscosity of rye dough during baking. A suspension of rye flour in water is heated at a constant rate and its change in viscosity as the starch gelatinises and as the starch gel is weakened by enzymic action is recorded as a graph. R. O. Brown

<sup>129</sup> *Cereal Chem.*, 1944, 21, 374; B., 1945, III, 61.

<sup>130</sup> *Ibid.*, 489; B., 1945, III, 125.

<sup>131</sup> T. R. Aitken, M. H. Fisher, and J. A. Anderson, *ibid.*, 465; B., 1945, III, 125.

<sup>132</sup> V. H. Morris, C. E. Bode, and H. K. Heizer, *ibid.*, 49; B., 1944, III, 180.

<sup>133</sup> *Ibid.*, 57; B., 1944, III, 180.

<sup>134</sup> *Ibid.*, 1945, 22, 134; B., 1945, III, 187.



and C. G. Harrel<sup>135</sup> found excellent correlation between the baking quality of rye flour and the maximum viscosity given by the Amylograph test. Inactivation of the enzymes of the flour by heating was found to increase the Amylograph viscosity figure and to improve the baking quality.

### MEAT.

During the year the investigations reported have again ranged widely and dealt with the composition of the raw material, the effects of preservation treatments, and the analysis of the products with special emphasis on the determination of vitamins.

The dressing-out percentage of beef from steers and heifers was found<sup>136</sup> to be directly related to the fatness of the animal but not to the percentage of muscular tissue, protein, or water. It was claimed that for maximum palatability about one third of the joint should be fat and that this optimum stage of fatness was obtained from animals dressing out at 58%. D. E. Walker and C. P. McMeekan<sup>137</sup> examined fat lambs, at 9 months old, of a number of breeds raised on New Zealand pastures and established the superiority of the Southdown cross breed. The poor keeping quality of beef from animals grazed in a certain part of Kansas and believed to be due to deficiency of phosphorus was investigated by J. L. Hall and co-workers.<sup>138</sup> They found that animals fed only on pasture grass which was low in phosphorus had a lower P:Ca ratio than normal, and had poor keeping qualities. These workers also investigated the characteristics of dark-cutting beef, the lean of which may vary in colour from brownish-red to purplish-black with corresponding loss of market value. Compared with ordinary beef, dark-cutting beef appears to have a high pH, low glucose, practically no glycogen, a rapid oxygen uptake, and, most significant, low lactic acid. P. C. Paul<sup>139</sup> noted that the tenderness, juiciness, flavour, and aroma of beef stored at 34—36° increased (as judged by tasting) for the first 9 days and then remained stationary or decreased slightly. Using roasting joints of pork loin, I. Noble and F. Hardy<sup>140</sup> found that the keeping properties were similar at 0°, 10°, and 15° F. over a period of 33 weeks; the flavour of the fat and desirability of aroma deteriorated more rapidly than other qualities, rendering the meat worse than "slightly desirable" after 16—22 weeks. On the other hand, tenderness and juiciness were apparently unchanged during the storage; this result for the juiciness factor obtained by tasting was confirmed by press fluid measurements.<sup>141</sup> R. L. Hiner, L. L. Madsen, and O. G. Hankins<sup>142</sup>

<sup>135</sup> *Cereal Chem.*, 1944, **21**, 360; B., 1945, III, 101.

<sup>136</sup> E. H. Callow, *J. Agric. Sci.*, 1944, **34**, 177; B., 1945, III, 104.

<sup>137</sup> *New Zealand J. Sci. Tech.*, 1944, **26**, A, 99; B., 1945, III, 105.

<sup>138</sup> J. L. Hall, H. W. Loy, D. L. Mackintosh, G. E. Vail, and C. E. Latschar, *Kansas Agric. Exp. Sta.*, 1944, *Tech. Bull.* 58.

<sup>139</sup> *Iowa State Coll. J. Sci.*, 1944, **19**, 50; B., 1945, III, 190.

<sup>140</sup> *Food Res.*, 1945, **10**, 165; B., 1945, III, 190.

<sup>141</sup> F. Hardy and I. Noble, *ibid.*, 160; B., 1945, III, 190.

<sup>142</sup> *Ibid.*, 312; B., 1945, III, 252.



have studied the effects of freezing  $1\frac{1}{2}$ -inch cubes of beef in still air at  $18^{\circ}$ ,  $0^{\circ}$ ,  $-10^{\circ}$ ,  $-40^{\circ}$ , and  $-114^{\circ}$  F.; the cubes were taken from the longissimus dorsi muscle of the short loin of carcasses chilled for 4 days at  $33-35^{\circ}$  F. Microscopical examination of sections showed that at  $18^{\circ}$  F. large interfibrillar areas of ice formed and pushed the fibres together but that as the freezing temperature was lowered, the size of the ice crystals and areas decreased. At  $0^{\circ}$  F. some intrafibrillar freezing and damage to the fibre wall occurred; this became more extensive at lower freezing temperatures until at  $-114^{\circ}$  F. fibres were even split longitudinally. Lowering of the freezing temperature also resulted in increased tenderness and decreased drip during thawing.

P. T. Zeigler and R. C. Miller<sup>143</sup> have reported on tests on the time required to cure hams by various treatments, expressing their results in days per inch of thickness. Using  $85^{\circ}$  pickle, frozen hams required 6 days, and frozen hams after thawing required 5 days per inch to reach the most desirable salt content; using  $75^{\circ}$  pickle 8 days per inch were required. Unchilled hams were dry-cured in 7 days per inch of thickness. The time of curing could also be shortened by pumping the hams with 8–10% of their weight of pickle. It was shown by W. H. White<sup>144</sup> that smoking retards the development of rancidity in the fat of bacon stored at  $-18^{\circ}$ ,  $-9^{\circ}$ ,  $-1^{\circ}$ , and  $7^{\circ}$ ; the fat of unsmoked bacon rancidified in 21–42 days, whereas after smoking the period was extended to 42–70 days. W. H. White, A. H. Woodcock, and N. E. Gibbons<sup>145</sup> found some indication that a maturation period of 10–15 days prior to smoking was the most suitable as judged by flavour, bacterial growth on the surface, peroxide formation in the fat, and the appearance of the lean. W. H. White, N. E. Gibbons, and M. W. Thistle<sup>146</sup> were prompted to investigate the keeping properties of hard cured bacon at  $60^{\circ}$  F. by the anticipated shortage of refrigerated space for shipping Canadian Wiltshire bacon to England. They found the most effective method to be packing in a 13 : 3 salt-borax mixture but considered that such treatment produced undesirable desiccation of the meat.

J. A. Pearce<sup>147</sup> found that little loss in palatability occurred in dehydrated pork kept in tinplate containers for a year at  $23.9-36.7^{\circ}$ , the effectiveness of packing material decreasing in the order tinplate, Reynolds' metal A-10, Dewey and Almy P.16, 300 M.S.T. Cellophane.

The choline and pyridoxine contents of various cuts of raw and cooked meat have been determined by J. M. McIntyre, B. S. Schweigert, and C. A. Elvehjem.<sup>148</sup> The muscle meats contained 0.22–0.48 mg. of pyridoxine per 100 g. and 70–144 mg. of choline per 100 g., while the offal meats results were higher. After cooking or curing 14–42% of

<sup>143</sup> *Pennsylvania Agric. Exp. Sta.*, 1942, *Bull.* 427; B., 1945, III, 105.

<sup>144</sup> *Canad. J. Res.*, 1944, 22, F, 97; B., 1945, III, 128.

<sup>145</sup> *Ibid.*, 107; B., 1945, III, 128.

<sup>146</sup> *Ibid.*, 1945, 23, F, 213; B., 1945, III, 230.

<sup>147</sup> *Ibid.*, 9; B., 1945, III, 146.

<sup>148</sup> *J. Nutrition*, 1944, 25, 219; B., 1945, III, 45.



the pyridoxine and 87—114% of the choline are retained. D. E. Brady, W. J. Peterson, and A. O. Shaw<sup>149</sup> found that the riboflavin contents of pork tenderloin and rib-eye muscle were  $1.21 \pm 0.09$  and  $2.75 \pm 2.0$   $\mu\text{g.}$  per g. and that on cooking about 80% was retained on a dry, fat-free basis. The aneurin contents were 13.9 and 15.1  $\mu\text{g.}$  per g. for the thoracic and lumbar regions of the rib-eye muscle and 14.8  $\mu\text{g.}$  per g. for the tenderloin; the retention of aneurin on cooking was 76—80% on the dry, fat-free basis. In beef, the same authors<sup>150</sup> found that 20 samples varied in riboflavin content over the range 1.20—2.28  $\mu\text{g.}$  per g., while tongue, spleen, liver, and heart contained respectively 3.07, 3.87, 27.2, and 10.7  $\mu\text{g.}$  per g. The retention of aneurin, riboflavin, niacin, and pantothenic acid on processing cured pork luncheon meat was studied by D. A. Greenwood, H. R. Kraybill, J. F. Feaster, and J. M. Jackson.<sup>151</sup> They found that a higher temperature for a shorter time was preferable to a longer time at a lower temperature; riboflavin and niacin were found to be heat-stable, but the rate of destruction of aneurin and pantothenic acid was doubled for a  $10^\circ$  rise in temperature. S. H. Jackson, A. Crook, V. Malone, and T. G. H. Drake<sup>152</sup> found that the variations in aneurin, riboflavin, and niacin contents were less between cuts from a single carcass, excepting the tenderloin, or between the left and right sides of a carcass than between different carcasses. The wet cure method of preparing bacon gave lower retentions of aneurin and niacin but a higher retention of riboflavin than the dry cure method.

### FISH.

The predominating feature of this year's publications has been the scientific investigation of the traditional methods of preserving fish—drying, salting, and smoking—while the publication of work on preservation by freezing and dehydration continues.

The changes in the composition and nutritional value of the common eel during growth have been determined by R. A. McCance.<sup>153</sup> Several chemical methods for determining the freshness or staleness of fish have been suggested. F. Charnley<sup>154</sup> found that the carbon dioxide value (measured in the Conway micro-diffusion apparatus) of the drained muscle tissue of canned salmon varied according to examiner's rating over the range 0.00—0.2 mg. of carbon dioxide per g. On the other hand, for lemon soles, H. L. A. Tarr<sup>155</sup> found this method less reliable than bacterial counts; with herrings too, this author found the method of doubtful value because fresh herrings may have a value 0.05 mg. of

<sup>149</sup> *Food Res.*, 1944, **9**, 400; B., 1945, III, 105.

<sup>150</sup> *Ibid.*, 406; A., 1945, III, 117.

<sup>151</sup> *Ind. Eng. Chem.*, 1944, **36**, 922; B., 1945, III, 63.

<sup>152</sup> *J. Nutrition*, 1945, **29**, 391; B., 1945, III, 209.

<sup>153</sup> *Biochem. J.*, 1944, **38**, 474; B., 1945, III, 77.

<sup>154</sup> *Analyst*, 1945, **70**, 14; C., 1945, 119.

<sup>155</sup> *Progr. Rept. Fish Res. Bd. Canada, Pacific Sta.*, 1945, No. 62, 7; B., 1945, III, 189.



carbon dioxide per g. of muscle and this value falls and then rises on storage, the fish becoming stale when the carbon dioxide value again reaches 0.05 mg. per g. F. Charnley and F. R. E. Davies<sup>156</sup> found some correlation between the examiner's assessment of freshness and the acid value of the oil of canned herrings. O. W. Lang, L. Farber, C. Beck, and F. Yerman<sup>157</sup> determined the amount of volatile odoriferous substances which could be aspirated from fish muscle press-juice by a current of air at a specified rate for a given time. The volatile substances were absorbed in alkaline permanganate, the permanganate not used being determined after acidification by addition of excess of ferrous ammonium sulphate and titration with ceric sulphate.

A useful review and a classification of the various kinds of smoked fish are given by C. L. Cutting<sup>158</sup>; the fish commonly smoked are herrings, haddock, and cod, the different products depending on the degree of salting, smoking, and drying. The contribution made by each of these treatments in preserving fish is discussed by J. M. Shewan.<sup>159</sup> This author concludes that salt exerts a definite preserving action only in the more heavily salted cures, *e.g.*, for red herring; in the lightly brined cures it helps in the formation of the pellicle and in the even smoking of the fish. Smoke has bactericidal properties and also imparts colour and flavour to the product; oak was found to be preferable to a number of other woods, the smoke derived from it containing aldehyde, ketones, acids, and phenols. E. P. Linton and H. V. French<sup>160</sup> devised a method for measuring the colour of fish and then attempted to correlate this with some readily determinable simple ingredient. The intensity of the colour of the extract obtained by simple extraction with a variety of solvents could not be correlated with the colour of the fish, which was, however, related to the colour of the clear extract obtained by digestion with 8% caustic potash. It was found that determination of formaldehyde, volatile organic acids, and acetone gave an unreliable index of smoke content, but that the estimation of volatile phenols was a satisfactory index of the degree of smoking. Some interesting analytical figures showing the changes that occur when haddock and herrings are smoked and when cod and herrings are salt-cured are given by J. M. Shewan.<sup>161</sup> The effect of these and other preservation treatments on the vitamin content of fish is discussed by J. A. Lovern<sup>162</sup> whilst C. L. Cutting<sup>163</sup> summarises what is known about the keeping properties of fish preserved by icing, by refrigeration, and by dehydration.

In the dehydration of fish by the normal method of air-drying cooked

<sup>156</sup> *Analyst*, 1944, **69**, 302; C., 1945, 41.

<sup>157</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 490; C., 1945, 41.

<sup>158</sup> *Chem. and Ind.*, 1945, 66; B., 1945, III, 104.

<sup>159</sup> *Ibid.*, 98; B., 1945, III, 127.

<sup>160</sup> *J. Fish. Res. Bd. Canada*, 1945, **6**, 338; B., 1945, III, 209.

<sup>161</sup> *Proc. Nutrition Soc.*, 1944, **2**, 105; B., 1945, III, 104.

<sup>162</sup> *Ibid.*, 100; B., 1945, III, 104.

<sup>163</sup> *Ibid.*, 113; B., 1945, III, 104.



minced fish on wire-mesh trays, O. C. Young<sup>164</sup> introduced a stage in which the cooked fish is pressed to remove expressible oil and water. H. L. A. Tarr<sup>165</sup> studied the changes in viable micro-organisms during the various stages of the dehydration process when applied to herring, ling cod, and coho salmon. Although most of the organisms were killed during the cooking, a progressive increase occurred subsequently during mincing and dehydration. When the dehydrated material was kept at 25° visible moulds grew only at relative humidity not less than 80%, corresponding with a moisture content of 16.8—18.3%, and bacterial growth occurred only at relative humidity not less than 85%. At relative humidity 65—80% the viable bacterial count decreased rapidly at first and then more slowly. In general there was an increase in total volatile bases and in trimethylamine at all relative humidity values that were too low for either bacterial or mould growth.

The work carried out at the Torrey Research Station on the preservation of herring by freezing and cold storage has been summarised by A. Banks.<sup>166</sup> The cold-storage life of herrings is limited by the development of rancidity in the fat; the oxidation of the fat is catalysed by an oxidative enzyme which is activated by salt and therefore freezing in an air blast is to be preferred to brine freezing. The deterioration of fish stored at -18° to -22° F. is notably less than that of fish stored at -4° F.

The nicotinic acid content of fish sold on the Calcutta market has been determined by B. de M. Braganca<sup>167</sup>; he found that the average figure for salt fish (3.1 mg. per 100 g. of muscle tissue) was higher than that for fresh-water fish (1.77 mg. per 100 g. of muscle tissue). W. S. Hoar and M. Barberie<sup>168</sup> studied the distribution of riboflavin in fresh and in processed fish. The riboflavin content of the skin was relatively high and that of the muscle low, while those of the liver and roe were intermediate. Fish contained less than 60% of the riboflavin found in meat. The riboflavin value was not affected by freezing, smoking, and drying treatment, but some loss occurred on salting and possibly on canning.

### EGGS.

The preparation and use of dried whole egg powder on a large scale has resulted in a continued output of papers concerned with its manufacture, storage, and properties. The conditions for freezing liquid egg and the drying of liquid egg on belts passing through an oven have been described briefly by A. E. Miller.<sup>169</sup> A flow diagram for the manufacture of dried egg powder together with an interesting table of instructions concerning temperature and humidity conditions, cleaning of plant, and general precautions required has been given by R. H. Carr and

<sup>164</sup> *Food in Canada*, 1944, 4, No. 10, 11; B., 1945, III, 106.

<sup>165</sup> *J. Fish. Res. Bd. Canada*, 1945, 6, 303; B., 1945, III, 209.

<sup>166</sup> *Food*, 1945, 14, 151; B., 1945, III, 189.

<sup>167</sup> *Ann. Biochem. Exp. Med.*, 1944, 4, 41; A., 1945, III, 117.

<sup>168</sup> *Canad. J. Res.*, 1945, 23, E, 8; B., 1945, III, 146.

<sup>169</sup> *Food*, 1945, 14, 10; B., 1945, III, 103.



G. Schild.<sup>170</sup> According to A. D. Bumashnov,<sup>171</sup> the conditions recommended for spray-drying whole egg are: temperature of inlet air 150—158°, temperature of air in region of atomisation 65—68°, final moisture content of powder 6—7%. The official U.S.A. standards are summarised by E. B. Heaton<sup>172</sup>; the egg solids content of dried whole egg should be not less than 92%, of dried egg yolk not less than 95%, and of liquid and frozen eggs not less than 43%.

It is claimed by R. C. Newton and L. D. Mink<sup>173</sup> that the reconstitution of the powder is improved by the addition to it of glycerol mono- or distearate or of the higher fatty acid esters of mono- or di-ethylene glycol having a free hydroxyl group. Another patent from the same source<sup>174</sup> claimed that the addition to the egg before drying of sodium lauryl, stearyl, or palmityl sulphate to the extent of 0.1—0.3% of the weight of the dried product aided the reconstitution of the powder and improved the whipping properties of the reconstituted material. J. R. Hawthorne<sup>175</sup> described a granular egg product, to be consumed as such or to be used as a component of a breakfast food, prepared by drying in a current of air at 60—90° minced, heat-coagulated whole egg loaded on to a wire tray at a rate of about 1½ lb. per sq. ft.

When dried whole egg powder was kept below 35° for periods up to 7 days little change occurred in either the intensity or quality of the colour, but above 35° the powder darkened, the magnitude of the change increasing with time and temperature.<sup>176</sup> Improvement in the keeping properties was also obtained by lowering the moisture content of the powder, but even at 1.4% moisture some deterioration occurred at 37° in 30 days and at 48° in 15 days. Packing in an atmosphere of carbon dioxide afforded some protection against heat deterioration, particularly of the solubility of the powder.<sup>177</sup> M. W. Thistle, W. H. White, D. A. Fletcher, and J. A. Pearce<sup>178</sup> found that the rate of deterioration, as assessed by the development of fluorescent material, was not influenced by the initial quality of the powder.

By using potassium chloride as a peptising agent and then salting out the denatured protein with sodium sulphate, E. H. McNally and J. Dizikes<sup>179</sup> determined the content of native protein in dried egg powder. In commercial powders the percentage of nitrogenous material in the native state ranged from 40 to 73% and decreased on storage. On

<sup>170</sup> *Food Ind.*, 1944, 16, No. 10, 84; B., 1945, III, 103.

<sup>171</sup> *U.S. Egg and Poultry Mag.*, 1944, 50, 312, 327, 356, 374, 381; B., 1944, III, 257.

<sup>172</sup> *Ibid.*, 1945, 51, 200, 230, 232; B., 1945, III, 189.

<sup>173</sup> Assrs. to Industrial Patents Corp., U.S.P. 2,182,209; B., 1945, III, 25.

<sup>174</sup> L. D. Mink, Assr. to Industrial Patents Corp., U.S.P. 2,183,515; B., 1945, III, 47.

<sup>175</sup> B.P. 564,772; B., 1945, III, 25.

<sup>176</sup> W. H. White and G. A. Grant, *Canad. J. Res.*, 1944, 21, F, 73; B., 1944, III, 232.

<sup>177</sup> M. W. Thistle, W. H. White, M. Reid, and A. H. Woodcock, *ibid.*, 80; B., 1944, III, 232.

<sup>178</sup> *Ibid.*, 1945, 23, F, 104; B., 1945, III, 145.

<sup>179</sup> *U.S. Egg and Poultry Mag.*, 1944, 50, 361, 379; B., 1944, III, 257.



storing dried egg powder S. E. Hartsel<sup>180</sup> noted that the total bacterial count decreased with time and with elevation of temperature of storage; yeast-water (1 part) and glucose tryptone agar (9 parts) is a suitable medium, and incubation at 32° is preferable to 37°. A formula has been devised by C. F. M. Fryd and S. W. F. Hanson<sup>181</sup> for obtaining the flavour score of dried egg from its physical and chemical properties. W. N. Lindsay and T. Mansfield<sup>182</sup> recommend drying 3-g. samples at 100° and 0.05 mm. in determining the moisture content of dried egg powder.

The vitamin-A content of dried egg was estimated by W. G. Schrenk, D. S. Chapin, and R. M. Conrad<sup>183</sup> by extraction with ether and measurement of the absorption in aqueous methanol solution at 3260 A. for vitamin-A and at 4500 A. for total yellow colour (due mainly to luteol and zeaxanthol); the optical density at 3260 A. is corrected by subtracting 15% of the optical density at 4500 A. S. M. Hauge, F. P. Zscheile, C. W. Carrick, and B. B. Bohren<sup>184</sup> found that the loss of vitamin-A when homogenised whole egg was dried commercially was negligible. On storage in cartons at temperatures not below 5° the loss of vitamin-A was small, but at 20° the loss was 30% after 3 months. The effect of drying and storing on the vitamins-A, -D, and -B<sub>1</sub>, riboflavin, and nicotinic acid present in egg was also studied by E. M. Cruickshank, E. Kodicek, and Y. L. Wang.<sup>185</sup> Little or no loss of vitamins-A and -D could be detected on drying or on storing the powder at 15° for 5 months; about 30% of the -B<sub>1</sub> was lost on drying, but no further loss occurred on storage. C. A. Denton, C. A. Cabell, H. Bastron, and R. Davis<sup>186</sup> found that emulsified whole egg and emulsified egg yolk contained respectively vitamin-A 50—61 and 95 i.u. per g. (biological method), 21—31 and 39 i.u. per g. (spectrophotometric method), vitamin-D 3.3—4.1 and 8.1 i.u. per g., and riboflavin 13—14 and 9 µg. per g. On spray-drying little loss of these vitamins occurred; during storage of the powder vitamin-D and riboflavin were found to be stable but the vitamin-A was rapidly destroyed, particularly at higher temperatures.

A. L. Romanoff and G. O. Hall<sup>187</sup> found that increase of radio-frequency conductivity is related to the deterioration of the egg; the conductivity increased with the age of the egg and the rate of increase was augmented by storage at higher temperatures. An efficient method for the preservation of table eggs is a flash heat-treatment (5 seconds at 100°) which forms a thin film of coagulated albumin adherent to the shell membrane<sup>188</sup>; the condition of eggs so treated was superior to that of untreated eggs

<sup>180</sup> *Food Res.*, 1944, **9**, 505; B., 1945, III, 126.

<sup>181</sup> *J.S.C.I.*, 1945, **64**, 55; B., 1945, III, 126.

<sup>182</sup> *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 628; C., 1945, 40.

<sup>183</sup> *Ibid.*, 632; C., 1945, 40.

<sup>184</sup> *Ind. Eng. Chem.*, 1944, **36**, 1065; B., 1945, III, 44.

<sup>185</sup> *J.S.C.I.*, 1945, **64**, 15; B., 1945, III, 76.

<sup>186</sup> *J. Nutrition*, 1944, **28**, 421; B., 1945, III, 103.

<sup>187</sup> *Food Res.*, 1944, **9**, 218; B., 1944, III, 232.

<sup>188</sup> A. L. Romanoff and A. J. Romanoff, *ibid.*, 358; B., 1945, III, 102.



similarly stored. F. P. Jeffrey and V. Darago<sup>189</sup> studied the effect of high humidity on the storage of eggs for short periods. At relative humidities of not less than 90% mould growth and musty taste appeared after 14 days unless forced draught was provided. The albumin quality was not affected by storage for 2—14 days at R.H. of 93—99%, 62—70%, or 78—82%.

#### MILK AND MILK PRODUCTS.

The general question of the control of milk quality has been reviewed by E. C. Thompson,<sup>190</sup> and J. L. Davies<sup>191</sup> has discussed plans for improvement in the production and handling of milk, whilst Sir W. Savage<sup>192</sup> has considered the milk supply from the bacteriological viewpoint. The 1944 Cantor lectures<sup>193</sup> dealt with (a) the requirements for better education in milk production and technology, (b) recent investigations concerning the use of oestrogenic and other hormones in relation to the initiation and stimulation of lactation and also the use of thyroxine and iodinated proteins for improvement of milk yield in declining lactation, and (c) recent aspects of the nutritive value of milk, including the effects of processing and the desirability of improving its nutritional quality. In a comprehensive study of the colour and flavour of Guernsey milk and their relation to the feed of the cow, J. W. Bartlett *et al.*<sup>194</sup> showed that milks with the highest colour and greatest ascorbic acid content had the best flavour.

G. H. Hartman and O. F. Garrett,<sup>195</sup> continuing their investigation of oxidised flavour in milk, have shown that there are three stages in the development of the flavour, characterised respectively by the following changes in the dissolved oxygen content: (a) a rapid fall, while the ascorbic acid present becomes oxidised; (b) an induction period of 2—5 hours while there is little change; (c) a slow fall due to oxidation of the fatty substance, during which the "off" flavour develops. The  $E_h$  of milk, shown previously to be related to the development of "oxidised" flavour, is, according to G. H. Hartman *et al.*,<sup>196</sup> increased by the presence of copper ions, and reduced by ferrous ions, by ascorbic acid, or by removal of dissolved oxygen (exposure to reduced pressure or by bubbling hydrogen through the milk). The presence of manganese has no effect on the tendency to develop "oxidised" flavour.<sup>197</sup> In the case of frozen cream, G. M. Trout and M. V. Scheid<sup>198</sup> showed that in accordance with earlier

<sup>189</sup> *New Jersey Agric. Exp. Sta.*, 1940, *Bull.* 682; B., 1945, III, 102.

<sup>190</sup> *Ind. Eng. Chem.*, 1945, 37, 208; B., 1945, III, 145.

<sup>191</sup> *Proc. Nutrition Soc.*, 1945, 2, 123; B., 1945, III, 207.

<sup>192</sup> *J. Roy. San. Inst.*, 1944, 64, 117; B., 1945, III, 126.

<sup>193</sup> E. Capstick, S. J. Folley, and S. K. Kon, *J. Soc. Arts*, 1945, 93, 106, 114, 122; B., 1945, III, 76.

<sup>194</sup> J. W. Bartlett, O. F. Garrett, R. P. Reece, and R. P. Hartman, *New Jersey Agric. Exp. Sta.*, 1940, *Bull.* 675; B., 1945, III, 101.

<sup>195</sup> *J. Dairy Sci.*, 1943, 26, 337; B., 1945, III, 42.

<sup>196</sup> G. H. Hartman, O. F. Garrett, and F. C. Button, *ibid.*, 515; B., 1945, III, 62.

<sup>197</sup> J. G. Archibald and H. G. Lindquist, *ibid.*, 325; B., 1945, III, 42.

<sup>198</sup> *Ibid.*, 609; B., 1945, III, 63.



indications this flavour is enhanced by copper contamination, while the tendency is reduced by homogenisation or by addition of sucrose, but high titratable acidity and variation in carotene content have little effect. The theory that increased lipolytic activity (which produces hydrolytic rancidity) occurring on agitation of milk is caused by increase in the fat-water interface has received support from the findings of T. Hlynka *et al.*<sup>199</sup>

In recent years it has been shown qualitatively that there is some connexion between the cooked flavour of heated milk and the presence of volatile sulphur compounds. R. C. Townley and I. A. Gould<sup>200</sup> have described an arbitrary method for determination of these sulphur compounds and showed that they are formed from the lactalbumin when the temperature exceeds 76—78° c. As the temperature is increased to 95°, the content increases but at higher temperatures it is reduced. The production of volatile sulphur compounds during the heating of milk has also been studied in relation to its pH, various added substances, traces of heavy metals, sunlight, homogenisation,<sup>200</sup> breed of cow, and period of lactation.<sup>201</sup>

The colour of evaporated milk is stated by R. W. Bell and B. H. Webb<sup>202</sup> to depend not only on the temperature and time of processing but also on some yet unknown property of raw milk. A. W. Turner<sup>203</sup> showed that the digestibility of milk is improved by enzyme action or by excessive heating treatment but is unaffected by pasteurisation, homogenisation, skimming or drying. A review of the high-temperature-short-time (H.T.S.T.) method of pasteurisation was made by E. R. Hiscox,<sup>204</sup> who indicated that the legalised procedure of heating at 162° F. for 15 seconds provides a good margin of safety as regards destruction of pathogenic organisms and that it is superior to the "holder" process in reduction of the number of thermophiles, but there is no evidence that it is less efficient against thermobacters as has been suspected in the U.S.A.

C. J. Koehn<sup>205</sup> has shown that the vitamin-A content of milk, which is highest in summer, depends on the succulence of the feed of the cows, and he suggests that by development of suitable winter forage it should be possible to extend to 8 months the period during which one quart of milk daily will furnish half an adult's requirement of vitamin-A. G. M. Trout *et al.*,<sup>206</sup> who studied the seasonal variation in the carotene content of cream, found that it was little affected by pasteurisation, homogenisation, or by the presence of copper. Irradiation of milk in

<sup>199</sup> T. Hlynka, E. G. Hood, and C. A. Gibson, *J. Dairy Sci.*, 1945, 28, 79; B., 1945, III, 207.

<sup>200</sup> *Ibid.*, 1943, 26, 689, 843, 853; B., 1945, III, 76, 101.

<sup>201</sup> R. C. Townley and I. A. Gould, *Mich. State Coll. Agric. Exp. Sta. Quart. Bull.*, 1943, 26, No. 1, 52; B., 1944, III, 257.

<sup>202</sup> *J. Dairy Sci.*, 1943, 26, 579; B., 1945, III, 62.

<sup>203</sup> *Food Res.*, 1945, 10, 52; B., 1945, III, 126.

<sup>204</sup> *J.S.C.I.*, 1944, 63, 298; B., 1945, III, 42.

<sup>205</sup> *J. Dairy Sci.*, 1943, 26, 673; B., 1945, III, 62.

<sup>206</sup> G. M. Trout, L. A. Moore, and M. V. Scheid, *ibid.*, 495; B., 1945, III, 63.



ultra-violet light caused loss of vitamin-A, carotene, and riboflavin, but the losses were small when the extent of irradiation was such that up to 400 U.S. units of vitamin-D per quart were produced.<sup>207</sup> Losses of riboflavin of approximately 4, 6, and 12% respectively occur during bottling, irradiation and pasteurisation of milk,<sup>208</sup> whilst exposure of bottled milk to sunlight may lead to destruction of as much as 60—70% of the riboflavin present and also rapid loss of ascorbic acid.<sup>209</sup> There was no loss of ascorbic acid or riboflavin and only 3% loss of aneurin during H.T.S.T. pasteurisation of milk at temperatures between 161° and 180° F. for 22 seconds.<sup>210</sup> F. J. Doan and D. V. Josephson<sup>211</sup> found that the loss of ascorbic acid during manufacture of evaporated milk was not correlated with the copper content or pH of the product, and that the loss during storage was greatest during the first two months. There was little reduction in the content of nicotinic acid, pantothenic acid, choline, and biotin during the preparation of irradiated evaporated or of dried milk.<sup>212</sup>

The calcium phosphate-casein complex in milk was found by G. A. Ramsdell and E. O. Whittier<sup>213</sup> to contain 4.8% of phosphate combined as the tricalcium salt (and not as calcium acid phosphate as stated by previous authors) and casein combined with 1.8% of calcium.

According to E. Kovacs,<sup>214</sup> it is possible to differentiate between the casein separated from milks of different species of animals by determination of the tyrosine, tryptophan, sulphur, and phosphorus contents, optical rotation, and ultra-violet absorption, but identification of the constituents of mixtures is not possible.

In a study of milk from the analytical point of view, O. R. Overman *et al.*,<sup>215</sup> reported the composition of 428 samples of milk from Brown Swiss cows. Determinations were made of the phosphatides in various dairy products by J. C. Crane and B. E. Horrall,<sup>216</sup> who found little variation in the amount present in the fat from the milk of different breeds of cows, but the results are only approximate as the method of determination used was admittedly of somewhat limited accuracy.

The methylene-blue reduction test applied to raw milk has been shown to be a measure of the velocity of growth and of the metabolic action of the bacteria present.<sup>217</sup> By comparison of the counts of moulds, yeasts,

<sup>207</sup> I. Fuhr, A. C. Dornbush, and W. H. Peterson, *J. Dairy Sci.*, 1943, 26, 643; B., 1945, III, 62.

<sup>208</sup> J. A. Ziegler and N. B. Keevil, *J. Biol. Chem.*, 1944, 155, 605; B., 1945, III, 62.

<sup>209</sup> A. D. Holmes and C. P. Jones, *J. Nutrition*, 1945, 29, 201; B., 1945, III, 145.

<sup>210</sup> A. D. Holmes, H. G. Lindquist, C. P. Jones, and A. W. Wertz, *J. Dairy Sci.*, 1945, 28, 29; B., 1945, III, 207.

<sup>211</sup> *Ibid.*, 1943, 26, 1031; B., 1945, III, 102.

<sup>212</sup> A. Z. Hodson, *J. Nutrition*, 1945, 29, 137; B., 1945, III, 145.

<sup>213</sup> *J. Biol. Chem.*, 1944, 154, 413; A., 1944, III, 818.

<sup>214</sup> *Biochem. Z.*, 1940, 306, 74; A., 1944, II, 384.

<sup>215</sup> O. R. Overman, O. F. Garrett, K. E. Wright, and F. P. Sanmann, *Illinois Agric. Exp. Sta.*, 1939, Bull. 457, 574; B., 1945, III, 108.

<sup>216</sup> *J. Dairy Sci.*, 1943, 26, 935; B., 1945, III, 102.

<sup>217</sup> T. Matuszewski and J. Supińska, *Zentr. Bakt.*, 1939, II, 101, 45; B., 1945, III, 17.



and bacteria, F. E. Nelson *et al.*<sup>218</sup> demonstrated that the development of one of these classes of micro-organisms in cream is not necessarily accompanied by the development of the others, but nevertheless, they concluded that the visual mould count has some limited value as a criterion of microbiological deterioration. According to F. W. Fabian and G. M. Trout,<sup>219</sup> greater reduction of the bacterial plate count of cream results when pasteurisation is effected by heating at 185° F. for five minutes than at lower temperatures for longer times. The count is increased with increasing pressure of homogenisation, but decreases when the cream is stored frozen for one year (at -5° to 10° F.). L. Gershenfeld and W. W. W. Ruthenberg<sup>220</sup> consider that the medium giving highest mould and yeast counts in dairy products is potato-glucose-agar at pH 3.3 (tartaric acid); they also discuss sources of contamination and methods of control. Pathogenic bacteria, which survive in milk for 1—7 weeks when the pH is reduced slowly to 3.9—4.2 by lactic fermentation, were more rapidly destroyed when lactic acid was added in one portion.<sup>221</sup> The development of a positive phosphatase test in pasteurised cream stored for 4 days at 4° or 10° was traced to the growth of *B. cereus* or *B. mesentericus*; this phosphatase was more active at pH 9.7 and more resistant to heating at 160° F. for 30 minutes than milk phosphatase.<sup>222</sup>

The keeping properties of block milk were improved by reduction of the  $E_h$  by addition of dextrose.<sup>223</sup> J. A. Pearce<sup>224</sup> found that chemical and physicochemical tests were inferior to palatability for assessing the quality of milk powder. For increasing the solubility of milk powder, the addition of a salt yielding a calcium salt less soluble than tricalcium phosphate (*e.g.*, oxalate or metaphosphate) has been advocated.<sup>225</sup>

Cheddar cheese has been the subject of several investigations. H. L. Wilson and co-workers<sup>226</sup> have emphasised that for the production of good-quality cheese, the desirable features are (1) use of raw milk of good bacteriological quality, (2) pasteurisation of the milk, (3) use of starters of constant activity added in limited quantities, and (4) slow fermentation to avoid development of acid and bitter flavour. W. H. Hoecket and B. W. Hammer<sup>227</sup> studied changes in the salt and moisture contents of the centre and exterior of cheese curd during pressing and their relation to the bacteriological condition and pH of the mass. The salt and moisture contents were almost equalised 72 hours after hooping, and were uniform

<sup>218</sup> F. E. Nelson, W. H. Martin, R. W. Morrison, and W. J. Caulfield, *J. Dairy Sci.*, 1943, **26**, 375; B., 1944, III, 231.

<sup>219</sup> *Ibid.*, 959; B., 1945, III, 102.

<sup>220</sup> *Amer. J. Pharm.*, 1944, **116**, 256; B., 1945, III, 44.

<sup>221</sup> F. L. Wilson and F. W. Tanner, *Food Res.*, 1945, **10**, 122; B., 1945, III, 188.

<sup>222</sup> F. W. Barber and W. C. Frazier, *J. Dairy Sci.*, 1943, **26**, 343; B., 1945, III, 43.

<sup>223</sup> O. J. Wouters, U.S.P. 2,319,362; B., 1945, III, 78.

<sup>224</sup> *Canad. J. Res.*, 1945, **23**, F, 177; B., 1945, III, 145.

<sup>225</sup> H. K. Salzberg, Assr. to Borden Co., U.S.P. 2,181,003; B., 1944, III, 261.

<sup>226</sup> H. L. Wilson, S. A. Hall, and L. A. Rogers, *J. Dairy Sci.*, 1945, **28**, 187; B., 1945, III, 207.

<sup>227</sup> *Food Res.*, 1944, **9**, 278; B., 1945, III, 44.



in the early stages of ripening. The soluble protein content increases during the ripening of cheese and the heat-stability (cooking quality) improves. The latter property is affected by the water and fat contents, the pH, and the temperature and duration of heating.<sup>228</sup> It has been demonstrated<sup>229</sup> that the phosphatase test may be applied to cheese curd to detect the presence of improperly pasteurised milk, but with aged cheese in which the pH has become low, false results may be obtained unless the cheese is macerated with a suitable buffer solution before testing: during the storage of cheese made from improperly pasteurised milk there is a small loss of phosphatase activity. Among new developments in cheese manufacture that have been suggested are (1) substitution of animal rennet by bacterial proteinases<sup>230</sup> or by an extract of chicken proventriculi<sup>231</sup>; (2) adjustment of the pH of the milk used to 6.6—7.4 by addition of calcium or magnesium oxide to give greater uniformity in processing and in flavour<sup>232</sup>; (3) modification of the soft curd in summer and autumn milk by addition of a little hydrochloric acid.<sup>233</sup> Addition to milk of whey cream (heated at 93° C. for 30 minutes to destroy bacteriophage) gave a larger yield of cheese with no deterioration in quality and caused no difficulty in manufacture.<sup>234</sup> According to an American patent<sup>235</sup> addition of dried mammary tissue improves cheese quality and shortens the ripening time, due to the action of lipolytic enzyme in the tissue. The development of acidity in pasteurised skimmed milk inoculated with lactic starters is stated to be maximum at 86° F.<sup>236</sup> The use of high scalding temperature (112—120° F.) and inoculation with starters containing *Str. thermophilus* and *L. bulgaricus* is claimed<sup>237</sup> to overcome the formation of pinholes which are a major problem in the manufacture of Brick cheese. The function and effect of the salts used in "melting" cheese for processed cheese manufacture have been investigated by H. J. Palmer and W. H. Sly,<sup>238</sup> who showed the superiority of sodium lactate containing a little trisodium phosphate; the use of calcium lactate, ammonium metaphosphate, and sodium ammonium pyrophosphate in this connexion has been patented.<sup>239</sup>

<sup>228</sup> C. Personius, E. Boardman, and A. R. Ausherman, *Food Res.*, 1944, **9**, 304; B., 1945, III, 43.

<sup>229</sup> W. J. Caulfield and W. H. Martin, *J. Dairy Sci.*, 1945, **28**, 155; B., 1945, III, 208.

<sup>230</sup> N. Evans and Rais, Ltd., J. L. Shimwell, and J. E. Evans, B.P. 565,788; B., 1945, III, 65.

<sup>231</sup> F. J. Babel, G. F. Stewart, and B. W. Hammer, *J. Dairy Sci.*, 1943, **26**, 331; B., 1945, III, 44.

<sup>232</sup> E. D. Fear, Assr. to I. E. Fear and H. Murphy, U.S.P. 2,326,132; B., 1945, III, 211.

<sup>233</sup> A. C. E. Smith, *J. Dept. Agric. Victoria*, 1942, **40**, 267; B., 1945, III, 169.

<sup>234</sup> H. R. Whitehead, *New Zealand J. Sci. Tech.*, 1944, **26**, A, 201; B., 1945, III, 76.

<sup>235</sup> C. B. Lane and B. W. Hammer, Assrs. to Iowa State Coll. Res. Found., U.S.P. 2,322,148; B., 1945, III, 148.

<sup>236</sup> N. S. Golding, H. Amundson, and R. O. Wagenaar, *J. Dairy Sci.*, 1943, **26**, 909; B., 1945, III, 101.

<sup>237</sup> J. G. Garey, E. M. Foster, and W. C. Frazier, *ibid.*, 833; B., 1945, III, 102.

<sup>238</sup> *J.S.C.I.*, 1944, **63**, 363; B., 1945, III, 17.

<sup>239</sup> J. D. Ingle, Assr. to Industrial Patents Corp., U.S.P. 2,317,958 and 2,319,187; B., 1945, III, 78.



Researches have been made in America on the substitution of sucrose by dextrose in ice cream. Up to 5% substitution had no effect on the physical properties of the mix (pH, viscosity, and specific gravity)<sup>240</sup> but 25% substitution reduced pH and viscosity slightly,<sup>241</sup> while 33% caused a detectable loss of sweetness.<sup>240</sup> The presence of dextrose leads to the formation of larger ice crystals and in such cases the use of a lower drawing temperature is recommended.<sup>240,242</sup> Comparative trials on palatability showed that, in the case of ice cream containing 16% of fat, the product containing sucrose and dextrose is preferable to that with sucrose alone, but the reverse holds in the case of ice cream with 12% of fat.<sup>241</sup> W. S. Mueller<sup>243</sup> attributes his finding that by ageing ice cream mix containing gelatin at 68° F. instead of at the usual 32—40° F. the gelatin has increased efficiency (giving a smoother product), to the formation of smaller micelles with more closely knit structure. It has been suggested<sup>244</sup> that improved flavour in ice cream results when mix standardised at 0.12% acidity is incubated with a "starter" culture until the acidity reaches 0.24%. According to L. R. Dowd and E. O. Anderson,<sup>245</sup> H.T.S.T. pasteurisation (180° F. for 19 seconds) of ice cream mix is as effective as heating at 160° F. for 30 minutes in reducing the number of bacteria, and does not impair the body, texture, and flavour of the product.

C. W. Decker and W. H. E. Reid<sup>246</sup> demonstrated three distinct stages in the growth of lactose crystals in ice cream during hardening and storage, namely, (1) initiation of crystallisation during the first 3—4 hours, (2) the "favourable" period of growth (12—24 hours) during which only a small proportion of the total lactose crystallises out, and (3) slow growth subsequently. These authors also showed that the crystals in processed cheese are composed of  $\alpha$ -lactose. Caking, in dried whey, is prevented by crystallising the lactose present in the form of monohydrate, which is facilitated by heating the liquid whey at pH 4.8 in order to precipitate the protein.<sup>247</sup>

#### EDIBLE FATS.

The work reviewed in this section may be classified under three headings, namely, (1) rancidity and deterioration of fatty foods; (2) butter; (3) vitamin-bearing oils.

<sup>240</sup> W. H. E. Reid and K. R. Minert, *Missouri Agric. Exp. Sta.*, 1942, *Res. Bull.* 339; B., 1945, III, 188.

<sup>241</sup> W. J. Corbett and P. H. Tracy, *Illinois Agric. Exp. Sta.*, 1939, *Bull.* 452, 346; B., 1945, III, 102.

<sup>242</sup> W. H. E. Reid and C. W. Decker, *Missouri Agric. Exp. Sta.*, 1943, *Res. Bull.* 370; B., 1945, III, 188.

<sup>243</sup> W. S. Mueller, *J. Dairy Sci.*, 1943, **26**, 189; B., 1945, III, 43.

<sup>244</sup> W. H. E. Reid and L. E. Smith, *Missouri Agric. Exp. Sta.*, 1942, *Res. Bull.* 340; B., 1945, III, 188.

<sup>245</sup> *J. Dairy Sci.*, 1943, **26**, 37; B., 1944, III, 231.

<sup>246</sup> C. W. Decker and W. H. E. Reid, *Missouri Agric. Exp. Sta.*, 1943, *Res. Bull.* 373; B., 1945, III, 188.

<sup>247</sup> D. D. Peebles and P. D. V. Manning, Assrs. to Western Condensing Co., U.S.P. 2,181,146; B., 1944, III, 261.



A discussion on the subject of flavours in food fats was presented by H. E. Robinson and H. C. Black,<sup>248</sup> both the desirable flavours and those produced by deterioration being considered. The prevention of oxidative rancidity by means of antioxidants and the dietary effects of rancid fats were also discussed.

The keeping properties of ration biscuits have of late years been a matter of great importance and it has been shown that the type and quality of the shortening used have more influence on the stability of the biscuits than the concentration of the fat or the method of manufacture of the biscuits. Increase in the fat concentration has a slight adverse effect on keeping quality when it is judged organoleptically, but this effect is not detectable by pH determinations or peroxide values of the fat.<sup>249</sup>

The question of flavour reversion in linseed oil shortening was carefully examined by J. G. Armstrong and W. D. McFarlane,<sup>250</sup> who concluded that the phenomenon was caused by some derivative or isomer of linolenic acid formed during hydrogenation, the "reverted" flavour being derived from this substance during baking. They proved that the unsaponifiable matter was not responsible and that the flavour could not be obtained from ethyl linolenate, except by adding it to an oil, such as sunflower seed oil, and hydrogenating the mixture. No method of avoiding the flavour reversion was discovered, but it could be reduced by various means such as the use of antioxidants or by extreme hydrogenation to a hard product (iodine value about 70) which could then be used as a constituent of a compound shortening. It has since been shown by O. S. Privett, R. B. Pringle, and W. D. McFarlane<sup>251</sup> that when linseed oil is polymerised by heating in a current of carbon dioxide at 270° C., about 60% of the product is soluble in acetone. This fraction may be hydrogenated and deodorised to give a shortening of good quality, showing no flavour reversion.

Ethyl gallate has been suggested as an effective antioxidant for preventing peroxide rancidity in stored fish, even when it is salted. Sodium gallate was not so effective.<sup>252</sup> The oxidative deterioration of food materials is said to be retarded by exposure to active hydrogen,<sup>253</sup> the food being passed through a discharge tube containing hydrogen or treated with metallic hydrides, such as calcium hydride, which react with the moisture present in the food.

The oxidation of vitamin-A and carotene in milk fat has been shown to coincide with the development of oily and tallowy flavours.<sup>254</sup> The

<sup>248</sup> *Ind. Eng. Chem.*, 1945, 37, 217; B., 1945, III, 146.

<sup>249</sup> G. A. Grant, J. B. Marshall, and W. H. White, *Canad. J. Res.*, 1945, 23, F, 123; B., 1945, III, 144.

<sup>250</sup> *Oil and Soap*, 1944, 21, 322; B., 1945, III, 76.

<sup>251</sup> *Ibid.*, 1945, 22, 287; B., 1946, II, 208.

<sup>252</sup> H. L. A. Tarr, *Nature*, 1944, 154, 824; B., 1945, III, 252.

<sup>253</sup> F. Kiefer, U.S.P. 2,318,867; B., 1945, III, 79.

<sup>254</sup> V. N. Krukovsky, G. H. Ellis, and W. R. Percy, *J. Dairy Sci.*, 1943, 26, 869; B., 1945, III, 102.



keeping quality of tinned butter at summer temperatures has been examined by E. G. Pont,<sup>255</sup> who found that though bacterial changes can be controlled by means of boric acid and salt, oxidative changes resulting in tallowiness can only be reduced by the use of an antioxidant, such as 0.02% of ethyl gallate. Reduction of air content and increase in pasteurisation temperature did not reduce the oxidative changes, which were found to be increased by copper contamination at as low a level as 0.06—0.17 p.p.m. No method was successful in preserving the butter sufficiently for use by the services in hot climates. The pro-oxidant effect of copper has also been noted in another paper,<sup>256</sup> in which it is pointed out that a high copper content may result, for example, from contact with unsuitable wrapping papers and that the induced bleaching and tallowiness may ultimately affect the whole of the butter.

An extensive review of the bacteriology of butter cultures has been made by B. W. Hammer and F. J. Babel.<sup>257</sup> As an explanation of slow acid production by butter cultures, the existence of an inhibiting principle showing the general characteristics of bacteriophage has been advanced.<sup>258</sup> It was isolated from bacteria-free filtrates of the cultures and was active against *Streptococcus lactis*. It was shown that the source of the milk was not a factor affecting the rate of acid production. No method was found for eliminating this principle without at the same time destroying the organisms of the butter culture. The effect of reworking unsalted butter on the growth of bacteria has also been investigated.<sup>259</sup> The butter was made from pasteurised cream and was held at  $-10^{\circ}\text{C}$ . Reworking caused an increased growth of all the bacteria tested, and the development of defects in the butter was accelerated. When a butter culture had been added to the cream, reworking caused a more rapid increase in pH, and the development of fatty acidity was increased by various lipolytic organisms. It was explained that reworking tends to aggregate the moisture droplets and provide a more available food supply for spoilage organisms. The growth of *Ps. putrefaciens* in butter results in the destruction of diacetyl and is responsible for cheesy and putrid flavours.<sup>260</sup> Other water bacteria have a similar effect.  $\beta\gamma$ -Butylene glycol and acetylmethylcarbinol are formed by the destruction of the diacetyl and the loss can be prevented by the addition of *Streptococcus lactis* to the cream before churning.<sup>261</sup> A patent on the production of diacetyl in butter cultures claims that the flavour of butter is enhanced by the addition to the cream of specially prepared cultures of *S. citrovorus* and *paracitrovorus*. These cultures are treated with citric acid or a

<sup>255</sup> *J. Counc. Sci. Ind. Res., Australia*, 1945, **18**, 53; B., 1945, III, 169.

<sup>256</sup> R. V. Hussong and B. W. Hammer, *Food Res.*, 1944, **9**, 289; B., 1945, III, 43.

<sup>257</sup> *J. Dairy Sci.*, 1943, **26**, 83; B., 1945, III, 43.

<sup>258</sup> F. E. Nelson, L. A. Harriman, and B. W. Hammer, *Iowa Agric. Exp. Sta.*, 1939, *Res. Bull.* 256, 217; B., 1945, III, 228.

<sup>259</sup> H. F. Long and B. W. Hammer, *ibid.*, *Res. Bull.* 263, 185; B., 1945, III, 228.

<sup>260</sup> P. R. Elliker and B. E. Horrall, *J. Dairy Sci.*, 1943, **26**, 943; B., 1945, III, 102.

<sup>261</sup> P. R. Elliker, *ibid.*, 1945, **28**, 93; B., 1945, III, 251.



mixture of the acid with dilute sulphuric acid to give a pH of 3.8—4.0 and allowed to ripen in the presence of an excess of air under a pressure of about 30 lb. per sq. inch.<sup>262</sup>

A simple and rapid laboratory method of churning cream into butter for mould mycelia determinations has been described in which the product was shown to give counts substantially the same as those obtained on butter manufactured commercially from the same cream.<sup>263</sup>

The series of papers from the University of Cape Town on South African fish products has been continued, the latest publications dealing with stockfish,<sup>264</sup> Cape John Dory,<sup>265</sup> and a number of miscellaneous South African fishes.<sup>266</sup> Data are given regarding distribution of the oil, seasonal variations, and vitamin-A and -D contents.

The large-scale production of liver oils from New Zealand fish has been described by M. M. Cunningham and C. Scott.<sup>267</sup> With livers of high oil content, such as shark, direct steam rendering with subsequent centrifuging is a satisfactory procedure, but when the oil content is low, a preliminary pepsin treatment is used. The plant and the processes are fully described and figures are given for yields, vitamin-A and -D contents, unsaponifiable matter, and free acidity of a number of different liver oils.

A process has been patented for improving the taste and odour of vitamin concentrates<sup>268</sup> in which the fish oil or fish oil stearin is added to a vegetable oil, the mixture being cooled slowly to obtain a deposit of stearin, which contains the bulk of the vitamins-A and -D. Suitable oils are teaseed or demargarinated olive or cottonseed oils. The product may be further purified by vacuum distillation.

#### COCOA, CHOCOLATE, AND CONFECTIONERY.

Further work by E. C. Humphries<sup>269</sup> on the changes undergone by cacao beans during the fermentation treatment has shown that in minced beans in presence of air autolysis due to the natural enzymes results in rapid decrease of the tannin content. He concludes that there are at least two tannin-like components: one that is readily oxidised, constituting about 4% by weight of the bean, the other (about 2% of the

<sup>262</sup> C. H. Werkman and B. W. Hamner, Assrs. to Iowa State Coll. Res. Found., U.S.P. 2,196,239; B., 1945, III, 256.

<sup>263</sup> H. H. Wilkowske and K. M. Renner, *J. Dairy Sci.*, 1943, 26, 283; B., 1945, III, 43.

<sup>264</sup> W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg, *J.S.C.I.*, 1944, 63, 313; B., 1945, III, 18.

<sup>265</sup> J. H. Corbett, W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg, *ibid.*, 371; B., 1945, III, 18.

<sup>266</sup> W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg, *ibid.*, 1945, 64, 61; B., 1945, III, 145.

<sup>267</sup> *New Zealand J. Sci. Tech.*, 1944, 26, B, 21; B., 1945, III, 18.

<sup>268</sup> K. C. D. Hickman, Assr. to Distillation Products, Inc., U.S.P. 2,326,644; B., 1945, III, 211.

<sup>269</sup> *Biochem. J.*, 1944, 38, 182; A., 1944, III, 612. *Trop. Agric., Trinidad*, 1945, 22, 67.



bean) being resistant to oxidation. In the absence of air an increase in tannin was found, indicating the presence of a tannin-precursor and showing that, unless the conditions of fermentation are mainly aërobic, an increase in tannin may result instead of the desired decrease. The same worker has studied the absolute changes that occur in the amount of some of the constituents during the 7-day fermentation that is normal in Trinidad, and reports losses of 11.2% of the original dry material, approximately 4% of the cacao butter, and up to 40% of the theobromine. As some losses of protein, of other nitrogenous substances, and of mineral salts also occur, he considers the process to be wasteful, and suggests that mincing of the beans, which in the presence of air results in rapid decrease in the tannin content, might form the basis of an alternative and less wasteful method.

Treatment of the cacao beans, prior to storage and transportation, by heating to 66° to destroy insect life and then compressing to a block to save space has been patented by A. W. MacIlwaine.<sup>270</sup> Removal of phosphatides from the beans by solvent extraction before roasting, in order to avoid formation of phosphatide decomposition products, or alternatively removal of these decomposition products after roasting of the beans, is advocated by H. Bresnick.<sup>271</sup>

Investigation of the unsaponifiable matter of the fat from cacao shell has been made by E. Ruppel,<sup>272</sup> who reports the presence of two nitrogen-containing fractions, one belonging to the cerebrin group. Sitosterol, stigmasterol, traces of ergosterol and sterol C (Lobert), ceryl alcohol, nonacosane, and a terpene were also found.

Three modified methods of "conching" chocolate to improve the taste, texture, and stability have been outlined. Two of these<sup>273</sup> describe apparatus whereby the molten material is beaten vigorously to obtain increased exposure to air. In the third<sup>274</sup> the chocolate is subjected to high-frequency vibration (about 15,000 per second) with or without simultaneous injection of air or oxygen, or oxidising or reducing gas mixtures. An electronic chocolate melter that will melt chocolate rapidly with no risk of overheating has been mentioned by F. W. Greer,<sup>275</sup> who considers that this method of melting may supersede the more conventional but slower melting in kettles.

Chocolate resistant to tropical temperatures is prepared, according to a patent granted to Sarotti A.-G.,<sup>276</sup> by addition to ordinary chocolate of substances that promote hardening when the mixture is heated. These include dextrose, whole or separated milk powder, and lactose. The mixture is processed and moulded in the normal way, and the bars

<sup>270</sup> B.P. 562,896; B., 1944, III, 214.

<sup>271</sup> U.S.P. 2,309,884; B., 1944, III, 214.

<sup>272</sup> *J. Pharm. Belg.*, 1943, 2, 26.

<sup>273</sup> P. Hollstein, U.S.P. 2,383,387. G. Lawton, U.S.P. 2,355,539.

<sup>274</sup> T. Nordenskjöld and K. S. Holmquist, B.P. 568,771; B., 1945, III, 175.

<sup>275</sup> *Manufg. Confect.*, 1945, 25, No. 5, 42.

<sup>276</sup> Ger.P. 744,862.



are then dried at 60—70° until the product will solidify when cooled to room temperature. A chocolate fondant coating for confectionery described by C. Veatch<sup>277</sup> is prepared from a syrup made from dextrose and glucose syrup to which are added cocoa powder, coconut oil, gelatin, and thin-boiling starch. The mixture is seeded with powdered dextrose at 43°, the setting of the coating being due to crystallisation of the dextrose, which must constitute not less than 50% by weight.

A greater increase in fluidity of products consisting of finely-divided solids dispersed in a fatty medium is stated to be obtained by the addition of 0.3% of methylated kephalin in place of the same quantity of lecithin.<sup>278</sup>

Definitions and standards of identity have been laid down by the U.S. Food and Drug Administration, Federal Security Agency,<sup>279</sup> for cacao products. Limits are given for added alkali, shell content, and fat contents of the various grades of cocoa, and for the minimum contents of chocolate liquor and milk solids in chocolates. Emulsifying ingredients, such as lecithin and related natural phosphatides and mono- and diglycerides of fat-forming fatty acids, must not exceed 0.5%, and their presence and that of alkali, spice, flavouring, or artificial flavouring must be declared on the label.

#### TEA.

Examination of a number of unblended black teas of Indian type has shown that the infusion as normally prepared contains riboflavin, averaging about 9  $\mu\text{g.}$  per g. of dry tea, a slightly lower value being found for China teas.<sup>280,281</sup> Two other vitamins of the B-group, namely, pantothenic acid<sup>280</sup> and nicotinic acid,<sup>282</sup> have also been found in tea in amounts ranging from 14 to 36  $\mu\text{g.}$  and 56 to 95  $\mu\text{g.}$  per g. of dry tea respectively.

After being subjected to fermentation in the presence of a manganese salt, an aqueous extract of the rough tea leaves cut from the bush in spring is said to contain the same quantity of tannins and caffeine as an extract from high-grade commercial tea.<sup>283</sup>

#### GENERAL FOOD ANALYSIS.

The analytical methods reviewed in this section are those that have not been reported in the preceding specialised sections.

Interest in the determination of traces of fluorine in foods has continued during 1945. The progress in the analytical methods for the determination of this element in foods has been recorded in these Annual Reports for the last two years<sup>284</sup>; a general survey of methods for the determination

<sup>277</sup> U.S.P. 2,188,489; B., 1945, III, 79.

<sup>278</sup> P. L. Julian, E. W. Meyer, and H. T. Iveson, U.S.P. 2,373,687.

<sup>279</sup> *Federal Register*, 1944, 9, 14,329.

<sup>280</sup> E. A. M. Bradford and E. B. Hughes, *Analyst*, 1945, 70, 2; C., 1945, 120.

<sup>281</sup> M. Kerly, *Biochem. J.*, 1944, 38, 423; A., 1945, III, 183.

<sup>282</sup> E. C. Barton-Wright, *ibid.*, 314; C., 1945, 46. E. B. Hughes and T. L. Parkinson, *Analyst*, 1945, 70, 86; A., 1945, III, 412.

<sup>283</sup> A. I. Oparin, *Biochimica*, 1944, 9, 90; B., 1945, III, 46.

<sup>284</sup> *Ann. Repts.*, 1943, 28, 406; 1944, 29, 444.



of traces of fluorine has now been made in the Annual Report for 1944 issued by the Chemical Society.<sup>285</sup> Recent communications of some interest have been made (a) on the determination of fluorine in organic compounds,<sup>286</sup> in which the precautions necessary for accurate results are considered; (b) on the accuracy of determination, without distillation, of amounts of fluorine of the order of 100—1000 p.p.m.<sup>287</sup>; and (c) on the determination of fluorine in bones<sup>288</sup>; in this paper an apparatus is described which is claimed to facilitate the distillation and titration of fluorine. An addendum<sup>289</sup> to the method recommended by the Society of Public Analysts and other Analytical Chemists<sup>290</sup> modifies the procedure for materials such as phosphates or foods rich in phosphates. It is recommended that two successive fractions of 150 ml. be distilled; if the second fraction shows an apparent fluorine content, the first 150-ml. fraction should be evaporated to dryness in the presence of calcium oxide and redistilled to give a 150-ml. fraction for the titration of fluorine.

Other work has been largely concerned with compilation of data on the amount of fluorine in foods. P. A. Clifford,<sup>291</sup> W. Harvey,<sup>292</sup> and S. Marcovitch<sup>293</sup> have reported on various items in American and British dietary. Clifford is of the opinion that many of the previous results published for the fluorine contents of foods have been much too high.

H. Fischbach has used vapour pressure measurements in order to find a more rapid and convenient method for the determination of moisture than that specified by the Quartermaster Corps of the U.S. Army. The first of two papers published deals with correlation of vapour pressure measurement with the amount of moisture in dehydrated vegetables<sup>294</sup>; the apparatus used is a modification of that of B. Makower and S. Myers referred to in these Reports last year.<sup>295</sup> Vapour pressure measurements are found by Fischbach to be independent of the particle size of the dried vegetable; the definite relationship between the moisture content and vapour pressure of dried vegetables is claimed by Fischbach to reflect more accurately the "state of wetness" of a dried vegetable than the percentage of moisture determined by a vacuum oven method. He also reports preliminary results which indicate that particle size has a definite effect on moisture determined by the method specified by the Quartermaster Corps, viz., drying 2 g. of the product in a vacuum oven at 70° for 6 hours at a pressure of not over 100 mm. The results obtained by

<sup>285</sup> *Ann. Repts. (Chem. Soc.)*, 1944, **41**, 283.

<sup>286</sup> P. Cattaneo and G. Karman, *Anal. Assoc. Quím. Argentina*, 1944, **32**, 127; C., 1945, 192.

<sup>287</sup> A. Schloemer, *Mikrochem.*, 1943, **31**, 123; C., 1945, 192.

<sup>288</sup> P. R. Godfrey and C. L. Shrewsbury, *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 335; C., 1945, 273.

<sup>289</sup> D. C. Garratt and D. D. Moir, *Analyst*, 1945, **70**, 442.

<sup>290</sup> *Ann. Repts.*, 1944, **29**, 445.

<sup>291</sup> *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 277; C., 1945, 254.

<sup>292</sup> *Nature*, 1945, **155**, 175.

<sup>293</sup> *Proc. Pacific Sci. Cong., Pacific Sci. Assoc.*, 1943, **6**, 125.

<sup>294</sup> *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 186; C., 1945, 183.

<sup>295</sup> *Ann. Repts.*, 1944, **29**, 446.



the use of vacuum oven and vapour pressure methods are to be correlated.<sup>296</sup> C. M. Johnson<sup>297</sup> has applied the Karl Fischer method to the determination of moisture in dry and dehydrated foods; he finds that the moisture contents thus determined (the titration being carried out electrometrically) were generally slightly higher than those obtained by the vacuum oven method. The method of determination of water in blood by means of calcium hydride has been extended to certain dried materials by P. W. Perryman,<sup>298</sup> who recommends extraction of the water with anhydrous dioxan; the volume of gas evolved, when the dioxan extract is allowed to react with calcium hydride, is measured in a graduated gas burette. It is pointed out that if a large amount of fat is present, this will be extracted by the dioxan and low results may be obtained; in this case a strictly uniform technique and empirical calibration curves should be used. The Brabender apparatus is recommended by H. Schmalfluss and H. Müller<sup>299</sup> for the determination of the moisture content of potato flakes and flour.

Some new methods for the determination of metallic traces in foods have been reported this year and some modifications of those already existing. A survey of methods for the determination of traces of zinc and arsenic is included in the report on Analytical Chemistry in the Annual Report of the Chemical Society for 1944.<sup>300</sup>

An outbreak of cadmium poisoning (involving 62 airmen) reported by G. G. Jenner and J. A. K. Cunningham<sup>301</sup> as due to fruit juice prepared in an urn with a galvanised interior again emphasises the necessity of care being taken in the choice of containers for acid products. In view of this occurrence the method of A. K. Klein and H. J. Wichmann<sup>302</sup> for the determination in foods of cadmium in the range 0—25  $\mu\text{g.}$ , with an accuracy of  $\pm 0.2 \mu\text{g.}$ , is of increased interest. Owing to the volatility of cadmium salts, even at  $500^\circ$ , wet digestion is preferable to dry ashing for destruction of the food material. After dilution of the digest, all "dithizone metals" are extracted, at pH 8.5, by dithizone in chloroform. Cadmium, zinc, stannous tin, lead, and bismuth are separated from mercury, copper, cobalt, and nickel by shaking with dilute hydrochloric acid. Cadmium dithizonate, with small amounts of zinc, is then quantitatively separated from this acid extract by shaking with dithizone after adding sufficient sodium hydroxide to give a concentration of 10% of free sodium hydroxide. A further washing of the dithizone extract with dilute hydrochloric acid is given, after which sodium hydroxide is added until 5% of free sodium hydroxide is present; the cadmium as dithizonate is then estimated

<sup>296</sup> *J. Assoc. Off. Agric. Chem.*, 1945, 28, 194; C., 1945, 258.

<sup>297</sup> *Ind. Eng. Chem. [Anal.]*, 1945, 17, 312; C., 1945, 253.

<sup>298</sup> *Analyst*, 1945, 70, 45; C., 1945, 146.

<sup>299</sup> *Z. Spiritusind.*, 1943, 66, 2.

<sup>300</sup> *Ann. Repts. (Chem. Soc.)*, 1944, 41, 272, 278.

<sup>301</sup> *New Zealand Med. J.*, 1944, 43, 282.

<sup>302</sup> *J. Assoc. Off. Agric. Chem.*, 1945, 29, 257; C., 1945, 254.



colorimetrically by means of a photometer. By this method the cadmium content of grapefruit juice (0.019 p.p.m.), spinach (0.09 p.p.m.), and kidneys from various animals (0.12—0.66 p.p.m.) was determined. Further investigation by the Association of Official Agricultural Chemists<sup>303</sup> of the method recommended in 1942 for the determination of copper<sup>304</sup> has shown that, although precipitation of bismuth as the basic salt is prevented in the presence of potassium iodide at pH 2, the extraction of copper with dithizone at this low pH is very slow; extraction after adjusting to pH 3.0—3.3 is therefore proposed. It was also found that decomposition products of dithizone are stripped from the solution together with copper; these are very resistant to destruction and give rise to erratic false blanks in the final estimation with carbamate. These false blanks are overcome by stripping the copper from the dithizone solution with slightly acid mercuric chloride, extracting the copper as carbamate from the mercuric chloride solution, evaporating to dryness, and heating with sulphuric and perchloric acids before final estimation as the carbamate.

The method reported last year<sup>305</sup> for the determination of small amounts of zinc in food in the presence of large amounts of interfering elements has been submitted to critical collaborative study<sup>306</sup>; it is considered to be satisfactory provided care is taken to avoid contamination with zinc from glassware, reagents, etc.

A detailed scheme has been published<sup>307</sup> for rapid determination of traces of arsenic, copper, lead, zinc, and iron successively in a single 2-g. sample of organic material. Although worked out specifically for medicinals, it is claimed that the scheme should be applicable to foods. The separation of the individual elements is achieved by solvent extraction of the metals as metallo-organic complexes; the final determinations are carried out photometrically by means of the Spekker photoelectric absorptiometer. The interference of other common metals (up to 500 p.p.m.) has been investigated; under the given conditions, the method is claimed to be specific for arsenic, lead, and iron. Bismuth interferes with the determination of copper, and cadmium is included with zinc; conditions are described for eliminating these interferences and for determining bismuth, nickel, and cadmium if desired. Results are reproducible on a 2-g. sample to  $\pm 0.5$ —1.0 p.p.m. in ranges up to 12.5 p.p.m. of arsenic (as  $\text{As}_2\text{O}_3$ ) and 25 p.p.m. of copper, lead, zinc, nickel, bismuth, or cadmium. D. Dickinson<sup>308</sup> proposes a rapid method for the determination of tin in which the food is ashed and the tin oxide

<sup>303</sup> C. A. Greenleaf, *J. Assoc. Off. Agric. Chem.*, 269; C., 1945, 254.

<sup>304</sup> C. A. Greenleaf, *ibid.*, 1942, 25, 385; B., 1942, III, 243.

<sup>305</sup> *Ann. Repts.*, 1944, 29, 447.

<sup>306</sup> L. V. Taylor and O. R. Alexander, *J. Assoc. Off. Agric. Chem.*, 1945, 28, 271; C., 1945, 254.

<sup>307</sup> N. Strafford, P. F. Wyatt, and F. G. Kershaw, *Analyst*, 1945, 70, 232; C., 1945, 284.

<sup>308</sup> *Ann. Rept. Fruit and Veg. Pres. Res. Sta., Campden*, 1944, 46.



reduced to tin by fusion with potassium cyanide. The tin is determined by colorimetric measurement of the red colour produced when dithiol is added to an acid solution of the melt. The only metal that interferes is copper, which can be removed by sodium diethyldithiocarbamate.

The metallic traces present in various food materials have been reported by various workers; e.g., dried parsley may contain up to 8 p.p.m. of arsenic<sup>309</sup>; grain (wheat, barley, or oats) dried directly with coke flue gas was not found to contain more than 0.2 p.p.m. of arsenic even when the coke contained as much as 80 p.p.m.<sup>310</sup>

The cobalt content of a number of food plants grown in various parts of the United States has been determined<sup>311</sup>; the results varied from 0.01 p.p.m. in field corn to 0.67 p.p.m. in spinach.

A rapid digestion method for the determination of phosphorus in foods has been reported,<sup>312</sup> by which a 500-mg. sample can be destroyed in 3—4 minutes using a perchloric-sulphuric acid digestion mixture with molybdenum (sodium molybdate) as a catalyst; the phosphorus is finally determined colorimetrically as the phosphomolybdate blue or as phosphovanadio-molybdate yellow.

Boron is determined, with an accuracy of 3% in amounts of 0.2—10  $\mu$ g., by colorimetric measurement of the red colour produced when an alcoholic solution of boric acid separated from the food is evaporated in the presence of trichloroacetic acid and turmeric.<sup>313</sup>

Work continues on the detection and determination of different chloroacetic acids proposed for use as preservatives, particularly in the U.S.A. J. B. Wilson<sup>314</sup> recommends a preliminary determination of the monochloroacetic acid content of commercial preservatives in view of the wide variation of concentration (6—60 g. of the acid per 100 ml. have been found). This is done by first determining the free chloride and then the total chlorine is determined by titration of excess of silver nitrate remaining after addition to an acidified (nitric acid) solution of preservative that has been hydrolysed completely by boiling with sodium hydroxide. From the difference in the two determinations, the amount of preservative can be estimated. An aliquot containing 50—100 mg. of monochloroacetic acid is then used for the accurate method already published,<sup>315</sup> which is the same in principle as that outlined above. A simplified method of detection of the preservative by means of the crystal characteristics of the barium salt is also given and in addition a chemical method, involving the production of indigo with anthranilic acid under specified conditions. It has also been noted<sup>316</sup> that the

<sup>309</sup> D. C. Garratt and W. W. Taylor, *Analyst*, 1945, **70**, 48; C., 1945, 129.

<sup>310</sup> C. R. Jones and E. C. Dawson, *ibid.*, 256.

<sup>311</sup> C. Hurwitz and K. C. Beeson, *Food Res.*, 1944, **9**, 348; A., 1945, III, 115.

<sup>312</sup> D. W. Bolin and O. E. Stamberg, *Ind. Eng. Chem. [Anal.]*, 1944, **16**, 345; C., 1944, 181.

<sup>313</sup> T. Philipson, *Lantbruks-Högskol. Ann.*, 1944–45, **12**, 251.

<sup>314</sup> J. Assoc. Off. Agric. Chem., 1945, **28**, 302; C., 1945, 275.

<sup>315</sup> J. B. Wilson, *ibid.*, 1944, **27**, 195; B., 1944, III, 163.

<sup>316</sup> W. V. Eisenberg, *ibid.*, 1945, **28**, 427; C., 1945, 275.



anhydrous instead of the hydrated barium chloroacetate sometimes separates out when the method of J. B. Wilson and G. L. Keenan is used<sup>317</sup>; the optical properties of this anhydrous salt can be used as an additional proof of the presence of monochloroacetic acid; the anhydrous salt is readily converted into the normal hydrated barium chloroacetate by crystallising from water. Dichloroacetic acid has been found as a preservative in 60% sugar syrups, sold in the U.S.A. C. F. Bruening suggests identification by means of the melting point of the *p*-toluidide prepared from dichloroacetic acid separated from the food by ether extraction, and determination by first hydrolysing the extracted acid with alcoholic potash and then estimation by Volhard's method of the chloride thus formed.<sup>318</sup>

0.05 mg. of *p*-chlorobenzoic acid can be detected in the presence of benzoic or salicylic acids or methyl *p*-hydroxybenzoate by extraction from food in the usual manner, nitration, and condensation with aniline after evaporation to dryness. After dissolving in hydrochloric acid, excess of sodium hydroxide is added; a characteristic blue-violet colour is given when *p*-chlorobenzoic acid is present, but cinnamic acid must first be removed if more than three parts to one of *p*-chlorobenzoic acid are present.<sup>319</sup>

A sublimation method for the determination of saccharin is recommended by M. Oakley.<sup>320</sup>

Preliminary studies by E. Eddings indicate that a malt vinegar pickle can be identified by determining the oxidation, iodine and ester values, and the bisulphite-binding compounds in the pickle liquor; identification of spirit and artificial vinegars may also be possible.<sup>321</sup>

The use of diphenyl-treated wrappers to prevent the rotting of citrus fruits is now allowed for fruit wrapped outside the United Kingdom<sup>322</sup>; the maximum amount permitted in orange wrappers is 40 mg. per 100 square inches. Methods have been published for the determination of diphenyl (and *o*-phenylphenol).<sup>323</sup> The absorption of diphenyl and *o*-phenylphenol by oranges is dealt with in this communication. From treated wraps containing 100 mg. of these substances, 100 g. of peel (approximately one orange) absorbed 4–20 mg. of diphenyl or 20–30 mg. of *o*-phenylphenol. F. C. Macintosh<sup>324</sup> shows that neither of these compounds is very toxic and the use of the wraps involves no danger to the health of the consumer.

The increasing use of DDT as an agricultural insecticide adds importance to methods for its determination, particularly in food materials

<sup>317</sup> *Ann. Repts.*, 1944, 29, 448.

<sup>318</sup> *J. Assoc. Off. Agric. Chem.*, 1945, 28, 620; C., 1946, 115.

<sup>319</sup> J. Deshusses, *Mitt. Lebensm. Hyg.*, 1944, 35, 1; C., 1946, 164.

<sup>320</sup> *J. Assoc. Off. Agric. Chem.*, 1945, 28, 298; C., 1945, 277.

<sup>321</sup> *Analyst*, 1945, 70, 49; C., 1945, 116.

<sup>322</sup> S.R.O., 1944, No. 1311.

<sup>323</sup> R. G. Tomkins and F. A. Isherwood, *Analyst*, 1945, 70, 330; B., 1945, III, 253.

<sup>324</sup> *Analyst*, 1945, 70, 334.



such as fruit. A review of the analytical methods for the determination of DDT is given in a communication on the chemistry of DDT by S. J. Cristol and H. L. Haller.<sup>325</sup> J. A. Fahey<sup>326</sup> outlines a technique for the recovery of organic chloride spray deposits from apple surfaces by means of an organic solvent such as benzene, ignition in a special apparatus of a volume of the solution containing chlorine equivalent to 0.5—5.0 mg. of DDT per ml., and recovery of the chlorine in a form suitable for quantitative estimation by a modification of the Volhard method. The method has the disadvantage that other organic chlorides extracted by the solvent would be estimated as DDT; this objection can also be raised against the method proposed by F. A. Gunter<sup>327</sup> by which the spray residue (isolated by benzene washing of the fruit etc.) is hydrolysed by alcoholic potash and the chlorine estimated by the Volhard method. The sensitivity is about 2 mg. of DDT per ml. of washings. A rapid colorimetric method<sup>328</sup> (for concentrations ranging from 0.001 to 0.01% of DDT) uses the Friedel-Crafts reaction to produce a compound with a stable colour, orange by transmitted light and greenish-orange by reflected light, which can be measured in a colorimeter.

A new chapter, under the heading "Extraneous Materials in Foods and Drugs," is to be published in the next edition of "Methods of Analysis A.O.A.C." Although the subject is not, strictly speaking, chemical analysis in the sense of the work dealt with in this report, it is of such importance to the industrial food chemist that it is felt that some mention should be made of the scope of the chapter and the work on which it is based. The chapter will deal with the detection by micro-analytical methods of filth such as rodent and insect contamination, dirt, splinters, hair, and fragments of metal and wood. A discussion of this subject as it affects foods, drugs, beverages and beverage materials, dairy products, nuts and nut products, baked products, cereals, eggs, confectionery, sugars, syrups, honey, vegetable products, spices, condiments, and miscellaneous products is given in a series of papers.<sup>329</sup> The United States Food and Drug Administration has also issued a circular<sup>330</sup> which deals in considerable detail with these methods of analysis and their application to plant and manufacturing control.

<sup>325</sup> *Chem. Eng. News*, 1945, **23**, 2070; B., 1946, III, 32.

<sup>326</sup> *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 152; C., 1945, 191.

<sup>327</sup> *Ind. Eng. Chem. [Anal.]*, 1945, **17**, 149; C., 1945, 191.

<sup>328</sup> E. L. Bailes and M. G. Payne, *ibid.*, 438; C., 1945, 269.

<sup>329</sup> *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 222.

<sup>330</sup> "Microanalysis of Food and Drug Products," U.S. Food and Drug Administration, *Food and Drug Circ. No. 1*, 1944.

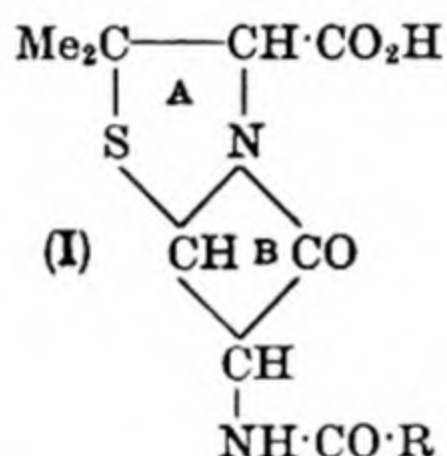


# FINE CHEMICALS AND MEDICINAL SUBSTANCES.

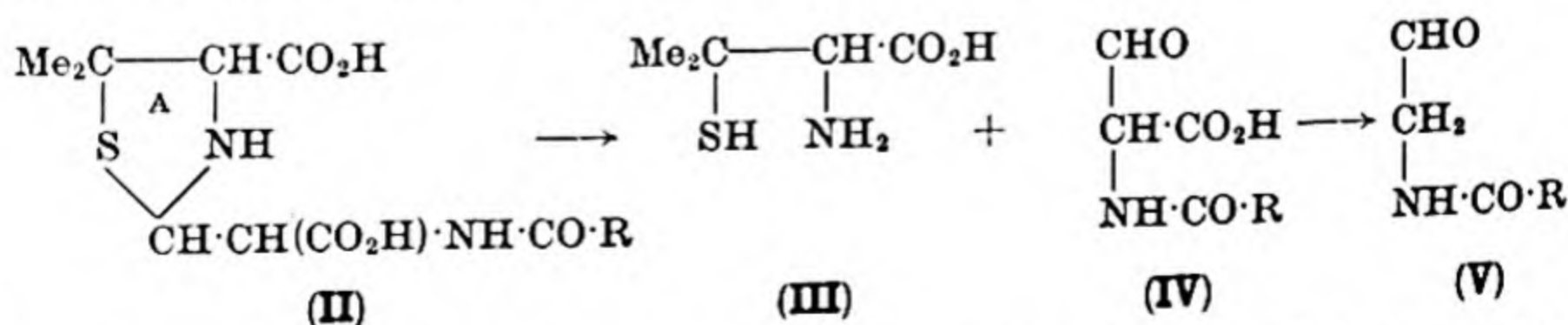
BY NORMAN EVERS, B.Sc., PH.D., F.R.I.C., AND  
N. R. CAMPBELL, B.Sc., PH.D., A.R.I.C.

## ANTIBIOTICS.

*Penicillin*.—At the time of writing this report only the bare facts of the constitution of penicillin have been published.<sup>1</sup> It is known that a vast amount of effort has been expended on the elucidation of the constitution and in hitherto unsuccessful attempts at the synthesis of penicillin. Many hundreds of compounds, a large proportion of which are of a type new to organic chemistry, have been prepared in the course of this work. It is known that a number of penicillins exist with a common structure differing only in the nature of a side-chain. The general formula is (I). The systems of naming the four penicillins are



different in this country and in the U.S.A. In England they are known as I, II, III, and IV, and in the U.S.A. as F, G, X, and K. The side-chains R are: I or F, pent- $\beta$ -enyl ( $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2$ ); II or G, benzyl; III or X, *p*-hydroxybenzyl; IV or K, *n*-heptyl. The remarkable feature of this structure is the  $\beta$ -lactam ring (B) which has not so far been found in any natural product. This ring is readily opened by alkali, primary alcohols and amines, cysteine, and the enzyme penicillinase and is the cause of the instability of penicillin. By the action of alkali penicilloic acids (II) are produced. By the action of mercuric chloride ring (A) is broken with the production of penicillamine (III) and penaldic acids (IV) which decompose into penilloaldehydes (V).

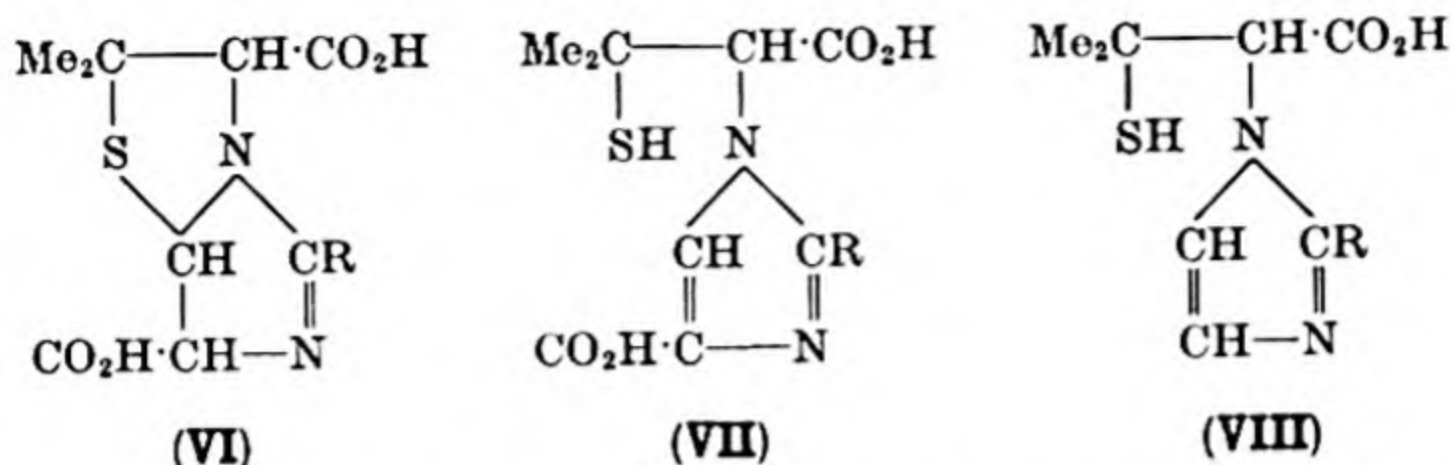


Penicillin in acid solution loses its biological activity and is converted into the isomeric penillic acids (VI), which with alkali gives isopenillic

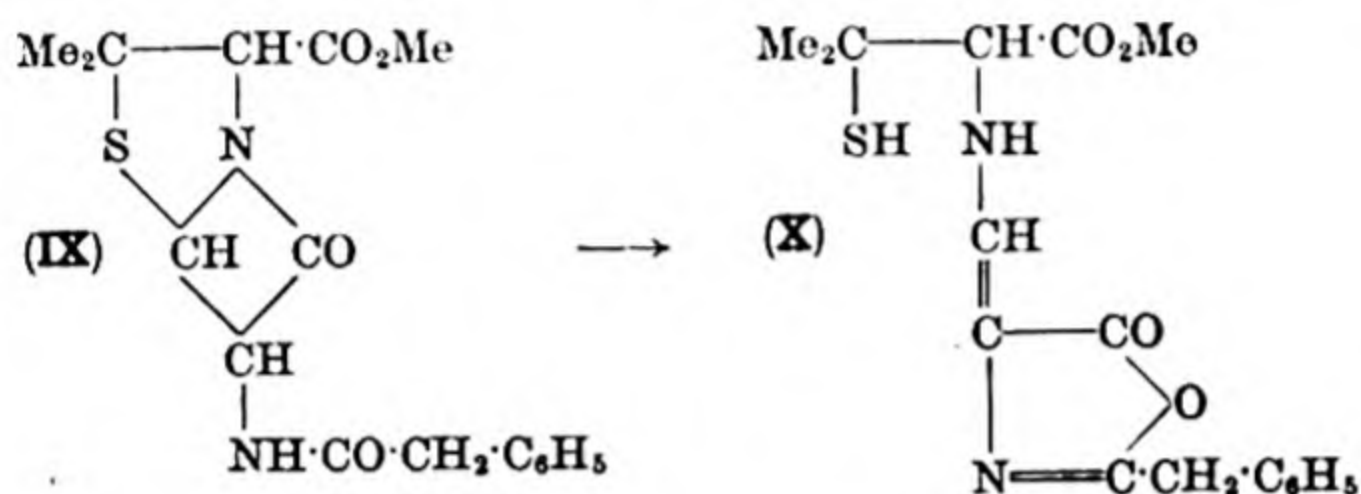
<sup>1</sup> *Nature*, 1945, 156, 766.



acids (VII) or with mercuric chloride forms penillamines (VIII). The penillic acids, isopenillic acids, and penillamines have all been synthesised.



The methyl ester of penicillin II (IX) has been converted by the action of mercuric chloride into the isomeric methyl ester of penicillenic acid (X).



The production of penicillin has shown marked progress. The original method of culture in small units such as milk bottles is being superseded by "deep" fermentation in large vessels of some 5000 gallons capacity. At the time of writing, two large factories in this country are coming into production. The U.S.A. production has increased enormously during the year.<sup>2</sup> In February, 1944, U.S.A. production was 18,700 mega (1 mega = 10<sup>6</sup> international units). In February, 1945, it was 405,000 mega, and in June, 1945, 647,000 mega. This large increase is in large measure due to the improved strains of mould which produce far more penicillin in the metabolite than the earlier ones. In Florey's original work he was obtaining 1—2 units per ml. of metabolite. Now 300 or more units per ml. are not uncommon. The purity of the final product has also been greatly increased and the sodium salt containing 150—200 units per mg. has been improved by better methods of extraction to 800—1000 or more units per mg.

The medium used is based on the corn steep liquor-lactose formula originally devised by Moyer and Coghill. The chemical changes which occur during submerged fermentation have been studied.<sup>3</sup> The addition of a number of chemicals in order to suppress the growth of other organisms in the medium has been tried.<sup>4</sup> Borax in 0.2% concentration was the only effective chemical which had no harmful effect on penicillin production.

<sup>2</sup> R. D. Coghill and R. S. Koch, *Chem. Eng. News*, 1945, 23, 2310; B., 1946, III, 119.

<sup>3</sup> H. Koffler *et al.*, *J. Bact.*, 1945, 50, 517.

<sup>4</sup> S. G. Knight and W. C. Frazier, *ibid.*, 505.



A method for concentrating penicillin solutions before freeze-drying known as the "drip thaw" method has been published.<sup>5</sup> The solution is frozen and allowed to thaw slowly so that the melted ice runs away. Over 90% of the penicillin is contained in the first fraction, which is about 50% of the original volume. Little has been published to suggest that any one of the penicillins is more effective than another clinically, but there is some evidence that penicillin III is more effective than penicillin II *in vitro*.<sup>6</sup>

*Streptomycin*.—This product of *Actinomyces* (or *Streptomyces*) *griseus* has proved to be the most promising of the antibiotics excluding penicillin. It is stated to be active against *M. tuberculosis*, but favourable reports on human subjects are still awaited. It is also active against certain Gram-negative organisms such as *E. coli*<sup>7</sup> as well as against Gram-positive organisms. Plants have been erected in the U.S.A. for the large-scale production of streptomycin, but so far there have been no reports of its being available in any quantity. The medium used for growing the organism consists of a source of nitrogen such as peptone, hydrolysed casein, or corn steep liquor with glucose or glycerin. The mould may be grown in deep culture as in the production of penicillin. The metabolite is treated with activated charcoal, which adsorbs the streptomycin. The charcoal is washed first with alcohol, then with anhydrous alcohol containing hydrochloric acid which elutes the streptomycin as chloride, which may be precipitated from the solution by the addition of anhydrous ether. It may be further purified by crystallisation as the relatively insoluble helianthate<sup>8</sup> or as reineckate.<sup>9</sup>

Streptomycin contains a guanidine group and a hydroxyl group but no amino-group. It is relatively stable. Its probable formula is  $C_{21}H_{37-39}O_{12}N_7$ . When streptomycin is hydrolysed in acid solution a base streptidine,  $C_8H_{18}O_4N_6$  is formed. It probably has the general constitution of a hydroxylated base linked glucosidically to a disaccharide-like molecule.<sup>10</sup>

Streptomycin is chemically and biologically much more stable than penicillin. Dilute sterile solutions maintain their activity for 15–17 days at 37°. It is not destroyed by other organisms. The unit of activity is based on the activity of 1  $\mu$ g. of pure streptomycin base.

*Miscellaneous Antibiotics*.—E. E. Hays *et al.*<sup>11</sup> have demonstrated the presence of an antibiotic in cultures of *Pseudomonas aeruginosa*, a fact

<sup>5</sup> S. W. Challinor and J. MacNaughton, *Nature*, 1945, 156, 602.

<sup>6</sup> R. L. Libby and N. L. Holmbegg, *Science*, 1945, 102, 304.

<sup>7</sup> S. A. Waksman and A. Schatz, *J. Amer. Pharm. Assoc.*, 1945, 34, 273; A., 1946, III, 493.

<sup>8</sup> F. A. Kuehl *et al.*, *Science*, 1945, 102, 34.

<sup>9</sup> J. Fried and O. Wintersteiner, *ibid.*, 101, 613. H. E. Carter, R. K. Clark, jun., S. R. Dickman, Y. H. Loo, P. S. Skell, and W. A. Strong, *J. Biol. Chem.*, 1945, 160, 337; A., 1946, III, 136.

<sup>10</sup> N. G. Brink, F. A. Kuehl, and K. Folkers, *Science*, 1945, 102, 507.

<sup>11</sup> *J. Biol. Chem.*, 1945, 159, 725; A., 1945, III, 893.



which had been suggested by some very early work of Whitehead and Wood in 1889. A number of compounds have been isolated and purified and at least four of them seem to be structurally related. They are active against Gram-positive but much less active against Gram-negative organisms.

M. A. Jennings and T. I. Williams<sup>12</sup> showed that the whole of the antibiotic activity of *Aspergillus effusus* could be accounted for by the kojic acid produced. Kojic acid is a weak antibiotic and a metabolic product of the growth of many species of *Aspergillus*. It has toxic effects when injected into animals. It is suggested that the antibiotic effects described from other species of *Aspergillus* are really due to kojic acid. This is denied by A. H. Cook and M. S. Lacey,<sup>13</sup> who state that *A. parasiticus* certainly produces antibiotic activity which is not due to kojic acid. Other reports on the presence of antibiotics active against *M. tuberculosis* have been made by J. M. Küring<sup>14</sup> (*A. ustus*) and I. E. Gerber and M. Gross.<sup>15</sup>

P. Kallós<sup>16</sup> has found antibiotic activity against *M. tuberculosis* in filtrates from pure cultures of a strain of *Aspergillus* (unidentified). Various workers have reported on the activity of *A. fumigatus* against *M. tuberculosis*. M. A. Jennings<sup>17</sup> suggests that this is due to helvolic acid, which has been previously described as a product of this mould. The same suggestion is made by I. N. Asheshov and F. Strelitz.<sup>18</sup> An antibiotic known as *flavicin* from *A. flavus* has been isolated in a fairly pure state by M. T. Bush, A. Goth, and H. L. Dickison<sup>19</sup> by multiple fractional extraction methods and chromatographic adsorption. It is stated to be very similar to penicillin.

*Bacillus subtilis* has been reported to contain an antibiotic which has been named *bacitracin* by B. A. Johnson, H. Anker, and F. L. Meleney.<sup>20</sup> It is chiefly active against Gram-positive organisms and against hæmolytic streptococcal infections in mice and gas gangrene in guinea-pigs. E. F. Jensen and D. J. Hirschmann<sup>21</sup> also describe an antibiotic from *B. subtilis* which they call *subtilin*.

A culture of *Penicillium brevi-compactum* was found by W. H. Wilkins and G. C. M. Harris<sup>22</sup> to inhibit the growth of *Staph. aureus*. H. W. Florey *et al.*<sup>23</sup> found that the substance responsible for the inhibition was mycophenolic acid, previously studied by P. W. Clutterbuck and H. Raistrick.<sup>24</sup>

<sup>12</sup> *Nature*, 1945, 155, 302; A., 1946, III, 859.

<sup>13</sup> *Ibid.*, 790; *Brit. J. Exp. Path.*, 1945, 26, 404; A., 1946, III, 493.

<sup>14</sup> *Science*, 1945, 102, 11.

<sup>15</sup> *Ibid.*, 101, 616.

<sup>16</sup> *Nature*, 1945, 155, 300; A., 1946, III, 859.

<sup>17</sup> *Ibid.*, 633.

<sup>18</sup> *Science*, 1945, 101, 120.

<sup>19</sup> *J. Pharm. Exp. Ther.*, 1945, 84, 262; A., 1946, III, 293.

<sup>20</sup> *Science*, 1945, 102, 376.

<sup>21</sup> *Arch. Biochem.*, 1944, 4, 297; A., 1945, III, 485.

<sup>22</sup> *Brit. J. exp. Path.*, 1943, 24, 141; A., 1944, III, 68.

<sup>23</sup> *Lancet*, 1946, 250, 46; A., 1946, III, 403.

<sup>24</sup> *Biochem. J.*, 1933, 27, 654.



E. P. Abraham<sup>25</sup> has now shown that *Staph. aureus* cultures rapidly adapted themselves to grow more easily in the presence of mycophenolic acid.

S. A. Waksman *et al.*<sup>26</sup> have found a new antibiotic substance *chætomin* from cultures of *Chaetomium cochloides*. It is present in much larger quantities in the mycelium than in the culture filtrate. It may be extracted from the mycelium by acetone or from the filtrate by ethyl acetate, and purified by washing with sodium bicarbonate and chromatographic adsorption. It contains nitrogen and sulphur but differs greatly in biological activity from gliotoxin and penicillin, though it acts mainly against Gram-positive organisms.

*Tyrothricin*.—J. C. Lewis, K. P. Dimick, and I. C. Feustel<sup>27</sup> obtained yields of tyrothricin in excess of 2 g. per l. of medium by growing *Bacillus brevis* in shallow layers for 10–16 days at 35°. The best media were prepared from acid hydrolysate of casein, corn steep liquor, tryptic digest of soya-bean meal, or press juice concentrates from waste asparagus butts as sources of nitrogen with 3–5% of glucose, mannitol, or glycerol.

*Tyrocidine*.—H. N. Christensen, L. Uzman, and D. M. Hegsted<sup>28</sup> have studied the amino-acid content of this polypeptide antibiotic; it is probably a peptide of eleven amino-acids.

*Gramicidin*.—The compound previously described by R. D. Dubos and R. J. Hotchkiss<sup>29</sup> is associated with tyrothricin and is also a polypeptide. The products of acid hydrolysis have been studied by H. N. Christensen and D. M. Hegsted.<sup>30</sup> It is probably not the same compound as gramicidin-S (see *Ann. Repts.*, 1944, 29, 452).

*Gliotoxin*.—The structure of this antibiotic has been investigated by J. D. Dutcher, J. R. Johnson, and W. F. Bruce.<sup>31</sup> Gliotoxin contains a disulphide linkage and reduction with aluminium gave a compound dethiogliotoxin containing no sulphur. Several alternative structures are proposed.

## VITAMINS.

*Vitamin-A*.—Claims to have produced synthetically compounds with vitamin-A biological activity have been made by N. A. Milas.<sup>32</sup> In one of these methods the aldehyde (I), originally prepared by Ishikawa and Matsuura,<sup>33</sup> was condensed with lithium acetylide in liquid ammonia at  $-60^{\circ}$  to  $-70^{\circ}$  to give the acetylenic carbinol (II), which when

<sup>25</sup> *Biochem. J.*, 1945, 39, 398; A., 1946, III, 314.

<sup>26</sup> *J. Bact.*, 1944, 48, 527, 531; A., 1945, III, 321.

<sup>27</sup> *Ind. Eng. Chem.*, 1945, 37, 996; A., 1946, III, 139.

<sup>28</sup> *J. Biol. Chem.*, 1945, 158, 279; A., 1945, II, 215.

<sup>29</sup> *J. Exp. Med.*, 1941, 73, 629.

<sup>30</sup> *J. Biol. Chem.*, 1945, 158, 593; A., 1945, III, 642.

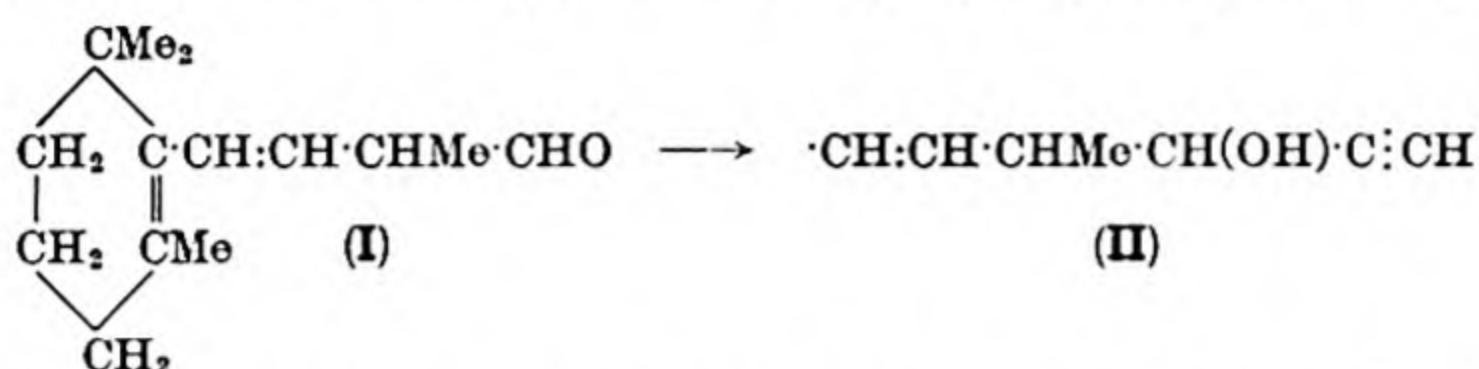
<sup>31</sup> *J. Amer. Chem. Soc.*, 1945, 67, 1736; A., 1946, II, 167.

<sup>32</sup> U.S.P. 2,369,156–2,369,168, 2,382,085–6.

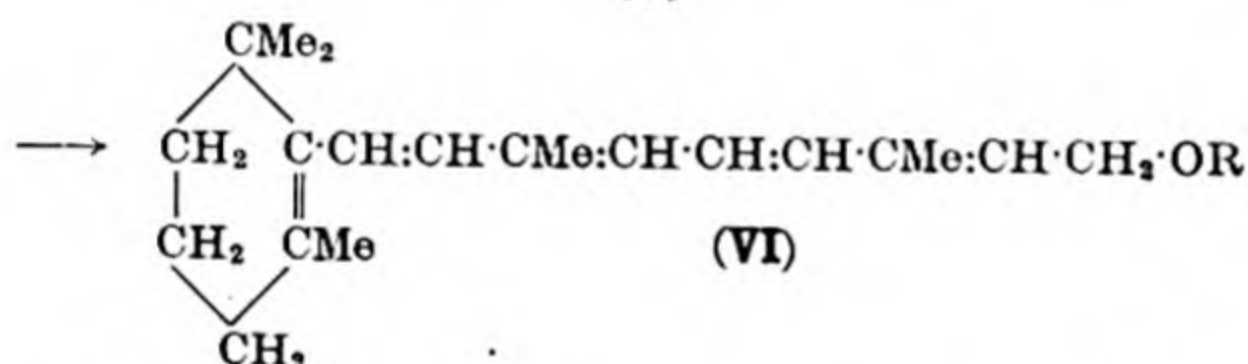
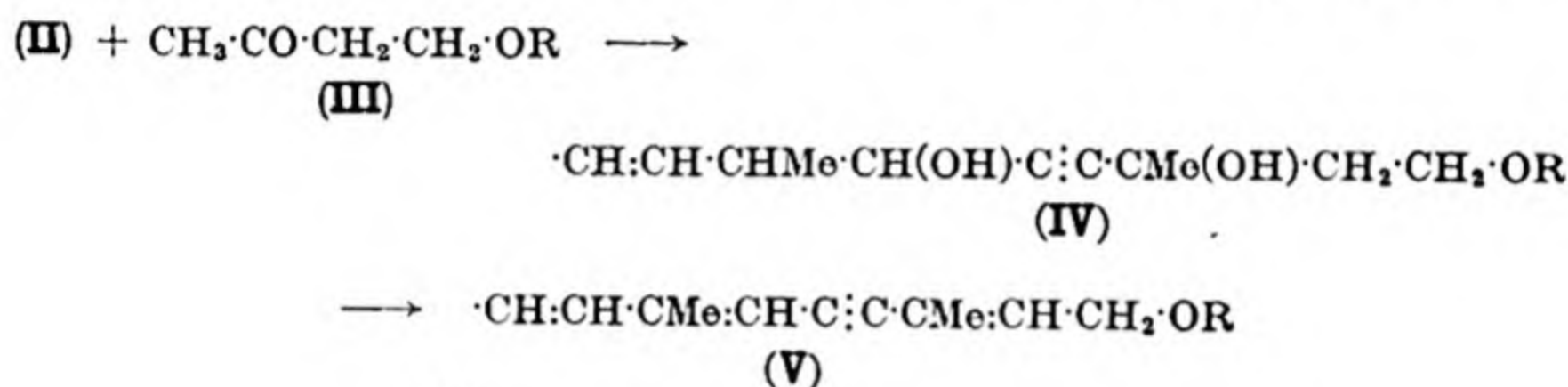
<sup>33</sup> *Sci. Rep. Tokyo Bunr. Daigaku*, 1937, A, 3, 173.



condensed by means of the Grignard reaction with the ketone (III) gives the acetylenic glycol (IV). This compound was dehydrated with *p*-toluenesulphonic acid to produce the polyvinylacetylene (V), which



when selectively hydrogenated yielded biologically active ethers or esters of vitamin-A (VI) depending on whether R in (III) is an alkyl or an acyl group. R. F. Hunter and N. E. Williams<sup>34</sup> claim to have effected the chemical conversion of  $\beta$ -carotene into vitamin-A in small yield by oxidative fission of the central double bond with hydrogen peroxide to



give vitamin-A aldehyde and subsequent reduction to vitamin-A alcohol. A new vitamin-A is described by C. D. Robeson and J. G. Baxter.<sup>35</sup> It was isolated from fish-liver oils and 30% and 33% of the vitamin-A in shark- and dogfish-liver oils respectively was found to consist of the new vitamin. It has an absorption maximum at 328  $m\mu$ ., whilst vitamin-A<sub>1</sub> has a maximum at 325  $m\mu$ . It gives a red anthraquinonecarboxylate (m.p. 130—131°), whereas that of -A<sub>1</sub> is yellow (m.p. 123—124°). It is suggested that it is a geometrical isomer of -A<sub>1</sub> differing in the *cis-trans*-configuration at the double bond nearest the hydroxyl group. Its biological potency is similar to that of vitamin-A<sub>1</sub>.

*Aneurin*.—D. S. Herr<sup>36</sup> reports the separation of aneurin from riboflavin by adsorption on acid-regenerated synthetic ion-exchange resins. Riboflavin is not adsorbed and the aneurin may be recovered by elution with strong acids. K. T. H. Farrer<sup>37</sup> has investigated the influence of buffer

<sup>34</sup> *J.C.S.*, 1945, 554; A., 1945, II, 398.

<sup>35</sup> *Nature*, 1945, 155, 300; A., 1946, II, 588; III, 935.

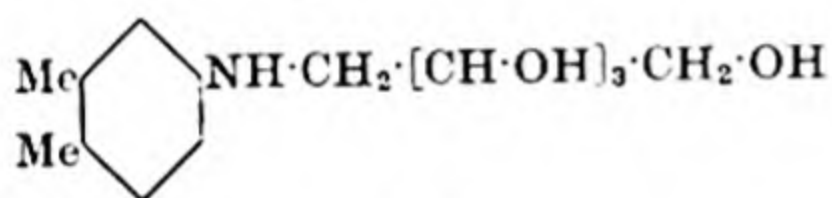
<sup>36</sup> *Ind. Eng. Chem.*, 1945, 37, 631; B., 1945, III, 212.

<sup>37</sup> *Biochem. J.*, 1945, 39, 128, 261; A., 1945, III, 627, 886.

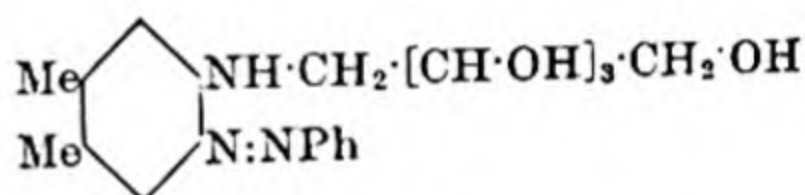


salts on the rate of destruction of aneurin at 100°. There is a linear relationship between the reaction velocity and the hydrogen-ion concentration which is different for each buffer. In all the buffers used the velocity of the reaction increased with rising pH. Cocarboxylase was more vulnerable to rising pH than aneurin.

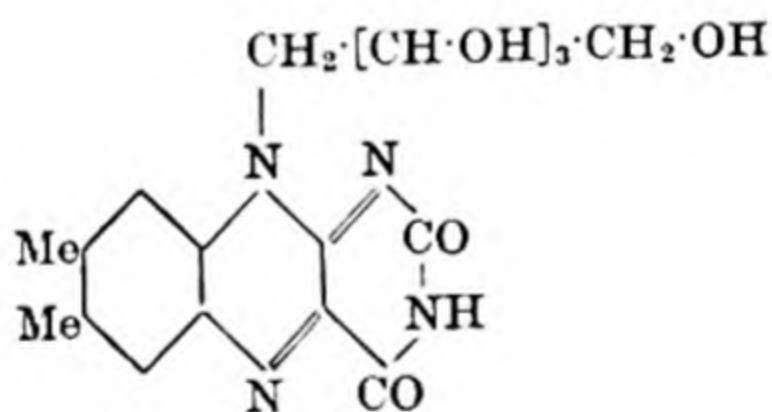
**Riboflavin.**—A method is described<sup>38</sup> for the concentration of riboflavin by adsorption on an inorganic adsorbent, *e.g.*, fuller's earth, and elution with aqueous acetone. Another patent<sup>39</sup> describes the recovery of riboflavin from fish press-water by adsorption on fuller's earth and elution with alcohol-pyridine. F. Bergel, A. Cohen, and J. W. Haworth<sup>40</sup> describe the synthesis of *N*-(*d*-ribityl)-*o*-4-xylydine (I), an intermediate in the synthesis of riboflavin. Acetylation of *d*-ribono-*o*-4-xylydide gave the tetra-acetyl compound, which on treatment with phosphorus pentachloride gives the corresponding imidochloride. Catalytic hydrogenation forms the acetylated secondary amine, which on deacetylation gives *N*-(*d*-ribityl)-*o*-4-xylydine; this compound was coupled with diazotised aniline giving 6-(*N*-*d*-ribitylamino)-3:4-dimethylazobenzene (II), which with alloxantin in the presence of palladised charcoal in an atmosphere of nitrogen produced riboflavin (III).



(I)



(II)



(III)

**Pyridoxine.**—The mode of action of pyridoxine has been made somewhat clearer in the last year. The suggestion was made by I. C. Gunsalus and others<sup>41</sup> that it is a constituent of the co-enzyme of tyrosine decarboxylase and by F. Schlenk and E. E. Snell<sup>42</sup> that it is a co-enzyme necessary for reactions involving transaminations. Pyridoxine (I) itself is inactive, but pyridoxal (II) is probably the active agent in these reactions. Pyridoxamine (III) is inactive in the former, but the co-transaminase activity seems in some way to be dependent on the inter-conversion of pyridoxal and pyridoxamine. Pyridoxal and pyridoxamine have together a greater stimulatory action on the growth of certain

<sup>38</sup> Borden Co., U.S.P. 2,186,314; B., 1945, III, 67.

<sup>39</sup> S. H. Lassen, and P. R. Park, Inc., U.S.P. 2,188,008; B., 1945, III, 82.

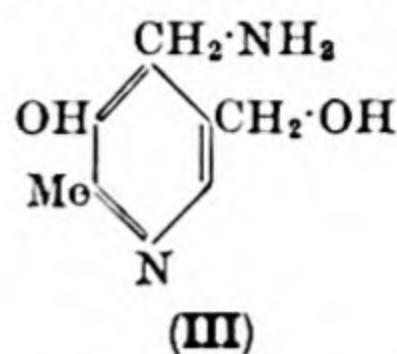
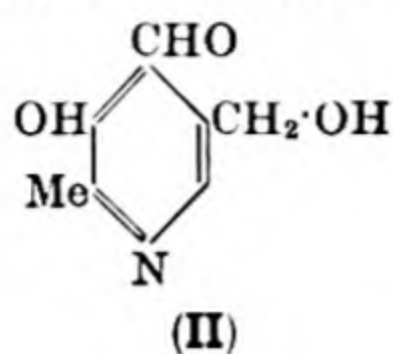
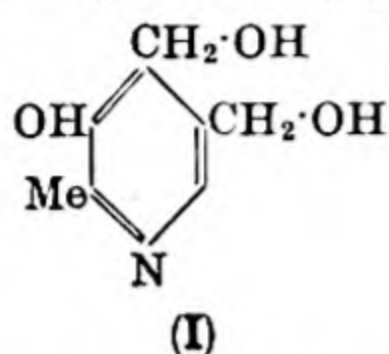
<sup>40</sup> J.C.S., '945, 165; A., 1945, II, 210.

<sup>41</sup> J. Biol. Chem., 1944, 155, 357, 557, 685; A., 1945, III, 127, 132, 197.

<sup>42</sup> Ibid., 1945, 157, 425; A., 1945, III, 478.



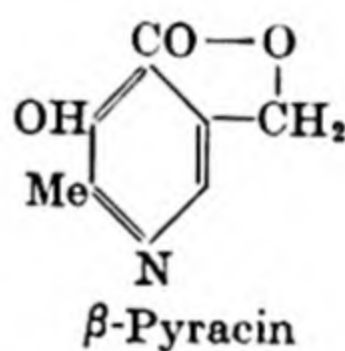
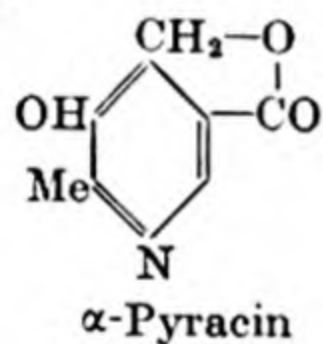
organisms than pyridoxine itself.<sup>43</sup> A method of synthesis<sup>44</sup> is claimed starting from 4-methoxy-3-methylisoquinoline, which is first oxidised to 3-methoxy-2-methylpyridine-4 : 5-dicarboxylic acid. This is converted



by way of the 4 : 5-dicyano-compound into 3-methoxy-2-methyl-4 : 5-bis(aminomethyl)pyridine. The methoxy-group is hydrolysed and by treatment with sodium nitrite pyridoxine is formed. Another method claimed<sup>45</sup> starts from 3-amino-2-methyl-5-aminomethyl-4-ethoxymethylpyridine. The ethoxy-group is replaced by halogen and hydrolysed to a hydroxy-group. The resulting compound is diazotised to pyridoxine.

The destruction of pyridoxine by light has been investigated by H. C. Epley,<sup>46</sup> who reports that the destruction becomes progressively more rapid as the wave-length of the light increases.

Two derivatives of pyridoxine,  $\alpha$ - and  $\beta$ -pyracin, have been shown to be essential with folic acid for the prevention of anæmia in chicks fed on a purified diet.<sup>47</sup>



**Folic Acid.**—The announcement has been made by R. B. Angier and others<sup>48</sup> of the synthesis of folic acid, but no details of its constitution or method of synthesis were given. T. D. Spies and others<sup>49</sup> showed that the administration of synthetic folic acid in macrocytic anæmia was followed by a striking hæmopoietic response. Folic acid had previously been identified with vitamin- $B_c$ , an anti-anæmia factor for the chick. It appears probable that there is some relationship between folic acid and xanthopterin, the yellow pigment of the brimstone butterfly. Both contain a high percentage of nitrogen. H. K. Mitchell<sup>50</sup> showed that the absorption spectrum of folic acid is similar to that of xanthopterin, and E. S. Bloom *et al.*<sup>51</sup> found this to be true of xanthopterin and vitamin- $B_c$ .

<sup>43</sup> E. E. Snell and A. N. Rannefeld, *J. Biol. Chem.*, 1945, **157**, 475; A., 1945, III, 379.

<sup>44</sup> L. J. Szabo, U.S.P. 2,359,260.

<sup>45</sup> Merck & Co., B.P. 557,804; B., 1944, III, 74.

<sup>46</sup> *Amer. J. Pharm.*, 1945, **117**, 265; A., 1946, III, 120.

<sup>47</sup> M. L. Scott, L. C. Norris, G. F. Heuser, W. F. Bruce, H. W. Coover, jun., W. D. Bellamy, and I. C. Gunsalus, *J. Biol. Chem.*, 1944, **154**, 713; A., 1945, III, 42.

<sup>48</sup> *Science*, 1945, **102**, 227.

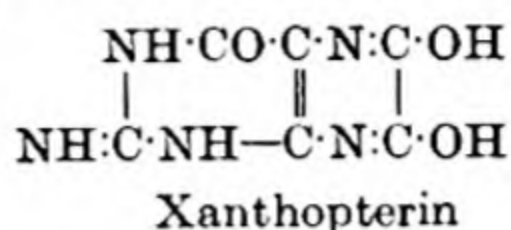
<sup>49</sup> *Sth. med. J.*, 1945, **38**, 707, 781.

<sup>50</sup> *J. Amer. Chem. Soc.*, 1944, **66**, 274; A., 1944, II, 244.

<sup>51</sup> *Science*, 1944, **100**, 295.



E. C. Barton-Wright, W. B. Emery, and F. A. Robinson,<sup>52</sup> in endeavouring to prepare a concentrate of folic acid from by-products obtained in the manufacture of a commercial liver extract, obtained

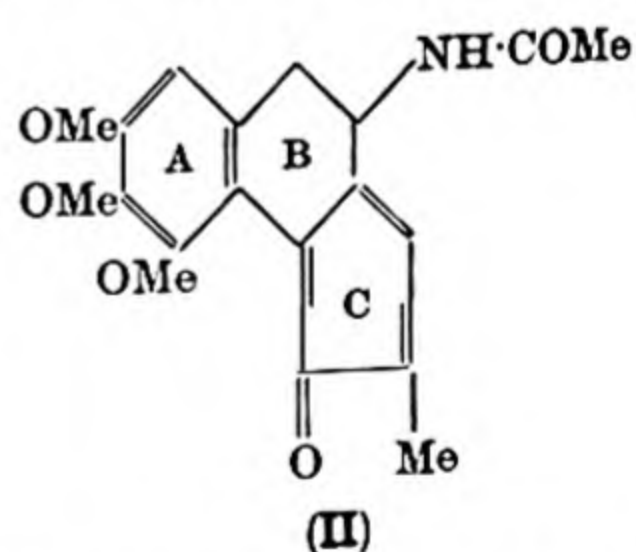
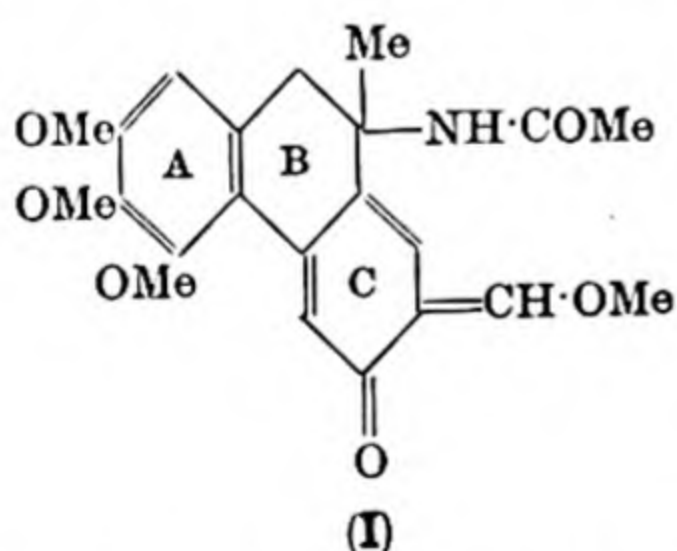


at least two other factors capable of stimulating the growth of *Lactobacillus helveticus* and *Streptococcus lactis*. Both factors were insoluble in chloroform; one was and the other was not adsorbed by Decalso.

### ALKALOIDS.

F. Mercier and J. Détrie<sup>53</sup> have reported on the properties of the camphorsulphonates of alkaloids of opium and the Solanaceæ, including melting points and specific rotations. H. F. W. Kirkpatrick<sup>54</sup> has studied the polarographic properties of alkaloids. While most alkaloids are not reducible, they produce catalytic waves which, though subject to great variation with changing conditions, can be used as a means of identification and determination if the conditions are carefully controlled. A more detailed study has been made of the alkaloids of the isoquinoline group. Optimum conditions are given for the polarographic determination of each alkaloid.

*Colchicine*.—The formula (I), originally proposed by Windaus<sup>55</sup> for colchicine, has been subjected to criticism recently. This structure has several unsatisfactory features, as pointed out by Cohen, Cook, and Roe,<sup>56</sup> who tentatively suggested that ring B might be seven-membered. Now there is a suggestion by M. J. S. Dewar<sup>57</sup> that ring c is seven-membered and formula (II) is put forward as representing colchicine.



*Quinamine*.—This alkaloid was isolated by Hesse in 1872, but has now been examined by T. A. Henry, K. S. Kirby, and G. E. Shaw.<sup>58</sup> Quinamine differs from all other cinchona alkaloids in that the quinuclidine

<sup>52</sup> *Biochem. J.*, 1945, **39**, 334; *A.*, 1946, III, 67.

<sup>53</sup> *J. Pharm. Chim.*, 1940, [ix], **1**, 287; *A.*, 1945, II, 262.

<sup>54</sup> *Quart. J. Pharm.*, 1945, **18**, 245, 338; *A.*, 1946, II, 57; *C.*, 1946, 31, 100.

<sup>55</sup> *Annalen*, 1934, **439**, 59.

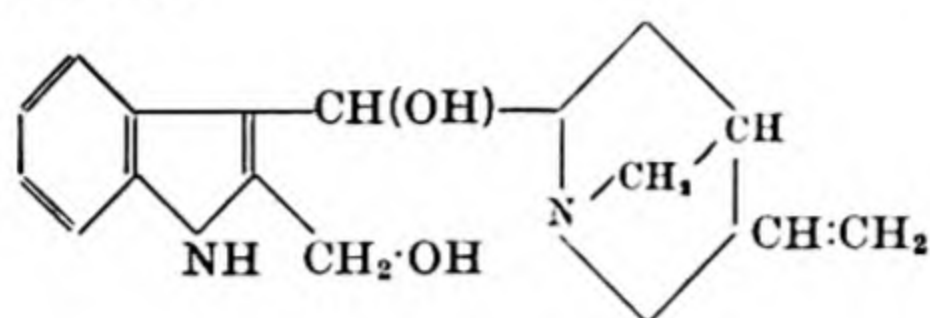
<sup>56</sup> *J.C.S.*, 1940, 194.

<sup>57</sup> *Nature*, 1945, **155**, 141, 479; *A.*, 1946, II, 408.

<sup>58</sup> *J.C.S.*, 1945, 524, 528; *A.*, 1945, II, 377.



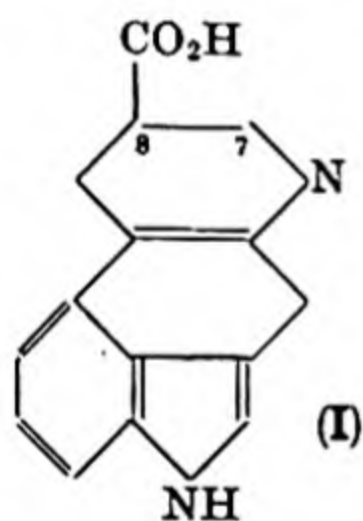
nucleus survives chromic acid oxidation, whereas no recognisable fragment of the second nucleus remains. These workers show that the second nucleus is indole in place of the quinoline nucleus present in all other cinchona alkaloids of known constitution. The probable structural formula of quinamine is :



*Delphinium Alkaloids.*—Two new alkaloids, *delphamine* and *condelphine*, have been isolated<sup>59</sup> from *Delphinium spp.*

M. V. Hunter<sup>60</sup> has examined the alkaloids of *D. ajacis* and obtained four crystalline and one amorphous alkaloids. Ajacine and ajaconine ( $C_{21}H_{31}O_3N$ ) were found and two new alkaloids, ajacine and ajacinoidine. A further base probably identical with lycoctonine (a product of hydrolysis of lycaconitine) was found. This is interesting in view of the many parallels between these alkaloids and the aconitine group. J. A. Goodson<sup>61</sup> has also found in *D. ajacis* ajacine, ajaconine, and three other bases.

*Ergot Alkaloids.*—A more rigid confirmation of the structure of lysergic acid (I) has been obtained by F. C. Uhle and W. A. Jacobs<sup>62</sup> by the synthesis of dihydro-*dl*-lysergic acid. Formerly there was some doubt as to whether the carboxyl group was at  $C_{(8)}$  or  $C_{(7)}$ . The preparation of hydrazides of dihydrolysergic acid and dihydroisolysergic acid has been claimed by A. Stoll and A. Hofmann<sup>63</sup> as intermediates in the preparation of synthetic ergot alkaloids. A method of preparation of ergometrine is described by M. R. Thompson<sup>64</sup> in which the total alkaloids of ergot are dissolved in a minimum amount of acetone and water is added to precipitate the water-insoluble alkaloids.



*Veratrine Alkaloids.*—A series of papers on these alkaloids has appeared in recent years from W. A. Jacobs and his colleagues.<sup>65</sup> All these bases are shown to be members of a closely related group which has also been found to include the potato base solanidine and related *Solanum* bases.

<sup>59</sup> M. S. Rabinovitsch and R. A. Konovalova, *J. Gen. Chem. Russ.*, 1942, 12, 321, 329; A., 1946, II, 239.

<sup>60</sup> *Quart. J. Pharm.*, 1944, 17, 302; A., 1945, II, 173.

<sup>61</sup> *J.C.S.*, 1945, 245; A., 1945, II, 262.

<sup>62</sup> *J. Org. Chem.*, 1945, 10, 76; A., 1945, II, 213.

<sup>63</sup> U.S.P. 2,359,688.

<sup>64</sup> U.S.P. 2,192,460; B., 1945, III, 178.

<sup>65</sup> *J. Biol. Chem.*, 1943, 148, 41, 51; 149, 271, 451; 1944, 152, 641; 155, 565; 1945, 159, 617; 160, 243, 555; A., 1943, II, 246, 313, 400; 1944, II, 65, 206; 1945, II, 71, 417; 1946, II, 111, 240.



The characteristic basic degradation product 3-methyl-6-ethylpyridine has been isolated from each on dehydrogenation. Solanidine has been shown to be a sterol derivative, and it is now clear that the whole veratrine group is closely related to the sterols. Further examination of the alkaloids of *Veratrum viride* has resulted in the isolation of a number of new alkaloids. Two of the *Veratrum* alkaloids, jervine and veratrosine, have been shown to be glucosides of  $\psi$ -jervine and veratramine respectively. In the course of this work sarsasapogenin was converted into dihydro-solanidine, which throws an interesting light on the way in which these steroidal alkaloids may be built up.

*Miscellaneous.*—W. G. C. Forsyth, S. F. Marrian, and T. S. Stevens<sup>66</sup> have started a re-investigation of the *Gelsemium* alkaloids. Gelsemine and sempervirine have been isolated in improved yields and gelsemicine, a secondary base, has been more fully characterised. Degradation experiments did not yield any characterisable products. H. Leuchs and H. Schulte<sup>67</sup> have prepared a third isomer of strychnine, isostrychnine II, by treating strychnine with red phosphorus and hydrobromic acid in boiling acetic acid and decomposing the filtrate from the hydrobromide of bromodeoxyisostrychnine so formed with aqueous ammonia and chloroform.

A method for the commercial synthesis of arecoline has been published by T. F. Dankova and others.<sup>68</sup> Ethyl  $\beta$ -chloropropionate and methylamine give methyldi- $\beta$ -carbethoxyethylamine, which by ring-closure gives ethyl 1-methyl-4-piperidone-3-carboxylate. By reduction this yields ethyl 4-hydroxy-1-methylpiperidine-3-carboxylate. Treatment with hydrochloric acid gives 1-methyl- $\Delta^3$ -tetrahydropyridine-3-carboxylic acid hydrochloride, which is esterified to arecoline.

#### STEROIDS AND RELATED SUBSTANCES.

*Bile Acids.*—W. M. Hoehn and J. Linsk<sup>69</sup> have converted cholic acid into the 7-keto-derivative by partial oxidation.

A simple degradation of the bile acid side-chain to the methyl ketone stage has been described by C. Meystre, H. Frey, A. Wettstein, and K. Miescher.<sup>70</sup> This is particularly noteworthy for its use of *N*-bromosuccinimide, a reagent which is suitable economically for preparative work, since good recovery of succinimide is possible. These authors claim a 25% overall yield of 3( $\alpha$ )-hydroxy-12( $\beta$ )-acetoxypregnan-20-one from 3( $\alpha$ ):12 $\beta$ -diacetoxy-24:24-diphenylchol-23-ene, by bromination in the allyl position, followed by dehydrobromination and chromic acid oxidation. No intermediates were isolated and a recovery of 68% of starting material was obtained.

<sup>66</sup> *J.C.S.*, 1945, 579; *A.*, 1946, II, 57.

<sup>67</sup> *Be.*, 1942, 75, [B], 1522; *A.*, 1945, II, 134.

<sup>68</sup> *J. Gen. Chem. Russ.*, 1941, 11, 934; *A.*, 1945, II, 416.

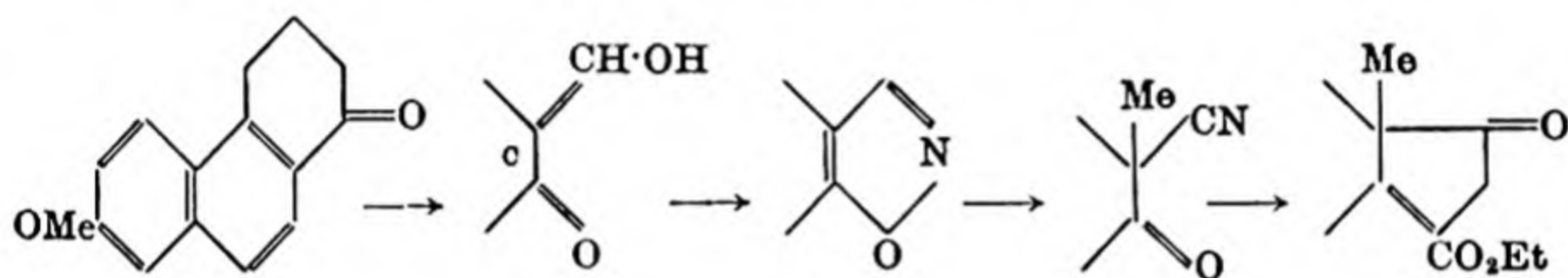
<sup>69</sup> *J. Amer. Chem. Soc.*, 1945, 67, 312; *A.*, 1945, II, 245.

<sup>70</sup> *Helv. Chim. Acta*, 1945, 27, 1815; *A.*, 1946, II, 330.



A further publication on the degradation of bile acid side-chains describes the reaction of the formates of bile acid chlorides with cadmium diphenyl to form phenyl ketones. This work, by W. Hoehn and R. G. Moffett,<sup>71</sup> covers, independently, the same ground as that of Jacobson, reported last year. This reaction has also been used by W. Cole and P. L. Julian,<sup>72</sup> who have commenced a new series of publications on the sterols, one avowed purpose of which is to provide more economical methods for degrading steroid side-chains.

*Æstrane Derivatives.*—A new synthesis of equilenin has been described by W. S. Johnson, J. W. Petersen, and C. D. Gutsche<sup>73</sup>; this involves fewer stages than the classical synthesis of Bachmann, Cole, and Wilds<sup>74</sup> and includes a novel reaction whereby in a single step 15-carbethoxy-14:15-dehydroequilenin was obtained from 2-cyano-1-keto-7-methoxy-2-methyl-1:2:3:4-tetrahydropheanthrene. This is of great interest, since a similar synthesis of œstrone is foreshadowed.



A. J. Birch, (Mrs.) R. Jaeger, and Sir R. Robinson<sup>75</sup> have prepared *dl-cis*-equilenin from the  $\alpha$ -norequilenin previously described by Koebner and Robinson.<sup>76</sup> The necessary methylation was effected by blocking the reactive methylene group at the 4-position by means of a methyl-anilinomethylene group, during methylation in the 2-position. It is claimed that *cis*-equilenin could be produced on a useful scale by this method.

Combined Intelligence Objectives Sub-Committee (C.I.O.S.) report<sup>77</sup> on the I.G. Farbenindustrie works at Elberfeld gives in some detail the complete synthesis of œstrone by a new method. 6-Methoxy- $\alpha$ -tetralone is condensed with acetylene, the product dehydrated and partially reduced to 6-methoxy-1-vinyl-3:4-dihydronaphthalene, which is then condensed with citraconic anhydride. The adduct is hydrogenated and the lactone hydrolysed and esterified with methyl alcohol. The resulting hydroxy-ester is converted into the bromo-ester, which is condensed with malonic ester and hydrolysed. Ring-closure of the resulting dicarboxylic acid gave a product containing œstrone methyl

<sup>71</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 740; *A.*, 1945, **II**, 325.

<sup>72</sup> *Ibid.*, 1369; *A.*, 1946, **II**, 38.

<sup>73</sup> *Ibid.*, 2274; *A.*, 1946, **II**, 327.

<sup>74</sup> *Ibid.*, 1940, **62**, 824.

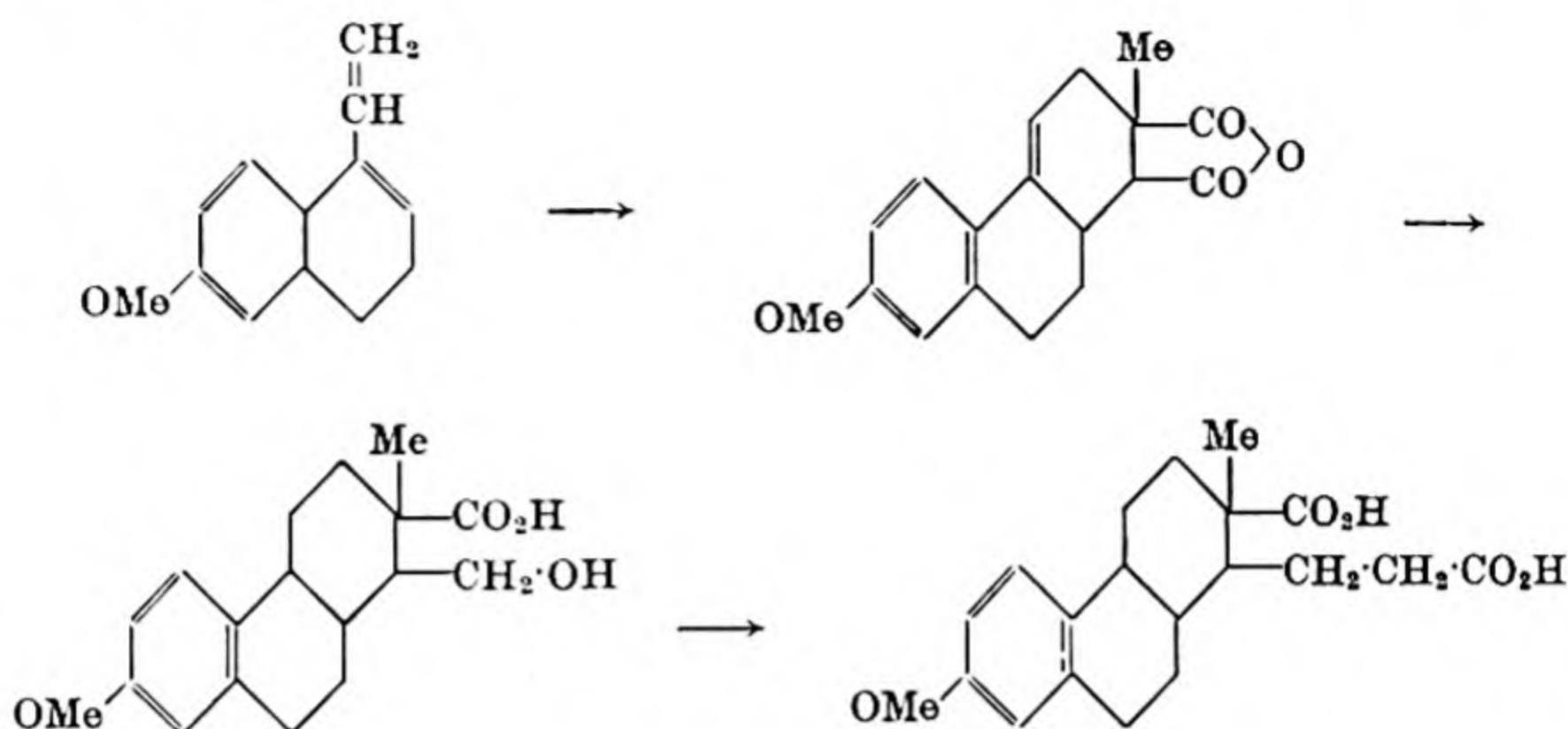
<sup>75</sup> *J.C.S.*, 1945, 582; *A.*, 1946, **II**, 36.

<sup>76</sup> *Ibid.*, 1938, 1994.

<sup>77</sup> *C.I.O.S.*, Item 24, File XXX-54, p. 20. (H.M. Stationery Office.)



ether, and demethylation produced a phenol having the oestrogenic activity of oestrone.



This synthesis, though possibly not suitable for development, is of interest particularly for the use of the Diels-Alder reaction to complete ring C, to introduce the angular methyl groups and to give suitable starting groups for the building of ring D.

K. Miescher<sup>78</sup> and his co-workers have commenced a study of the carboxylic acids derived from natural oestrogens by Marrian and Haslewood<sup>79</sup> and by Doisy.<sup>80</sup> The dicarboxylic acid originally obtained from oestriol has now been obtained by oxidation of the benzyl ester of oestrone; it has been named marrianolic acid and its constitution confirmed as 2-carboxy-7-hydroxy-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-1-acetic acid. Of greater interest is doisynolic acid, obtained by fusion of oestradiol with alkali, and shown to be 7-hydroxy-1-ethyl-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylic acid. This acid is a highly active oestrogen exceeded in activity by its bis-dehydro-derivative prepared from the benzyl ether of equilenin. Bis-dehydrodoisynolic acid has also been completely synthesised.

*Androstane Derivatives.*—An improved method for preparing 16-iso-propylideneandrost-5-en-3-ol-17-one from *trans*-dehydroandrosterone acetate has been given by W. C. J. Ross.<sup>81</sup>

A C.I.O.S. report on N. V. Organon<sup>82</sup> gives the information that the oxidation of cholesterol acetate dibromide to dehydroisoandrosterone is now being carried out with 50% increased yield by using a mixture of acetic acid and ethylene dichloride as solvent. This revised process gives no pregnenolone acetate as a by-product.

<sup>78</sup> *Helv. Chim. Acta*, 1944, **27**, 1727; 1945, **28**, 156, 991, 1342; A., 1946, II, 85, 202, 329.

<sup>79</sup> *J.S.C.I.*, 1932, **51**, 277.

<sup>80</sup> *J. Biol. Chem.*, 1933, **99**, 327.

<sup>81</sup> *J.C.S.*, 1945, 25; A., 1945, II, 121.

<sup>82</sup> *C.I.O.S. Item 24, Files X-14—XII-23.*

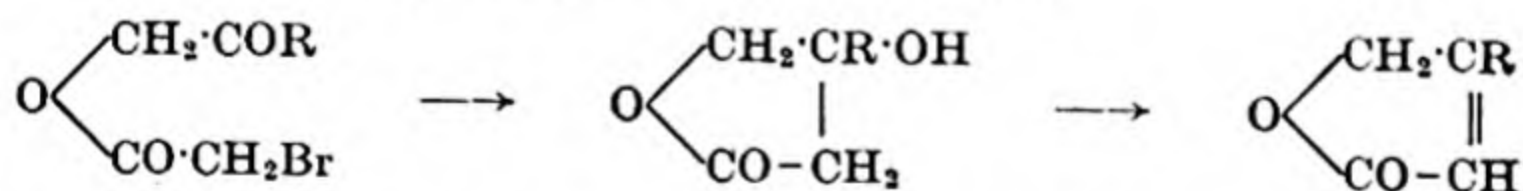


*Pregnane Derivatives.*—W. C. J. Ross<sup>83</sup> has prepared a series of simple aromatic methyl and acetoxymethyl ketones, derived from stilbene, dibenzyl, and triphenylethylene; these ketones, designated as synthetic analogues of progesterone and corticosterone, have been prepared in most cases by Friedel-Crafts condensation of acetyl or chloroacetyl chloride with aromatic hydrocarbons, followed in the latter case by reaction with potassium acetate. Probably the most interesting of these series are the two 4:4'-disubstituted diethyldibenzyls, which may be regarded as variants of "hexœstrol." No biological tests are reported on the progesterone analogues, and the corticosterone analogues have shown no marked activity in preliminary tests on adrenalectomised rats.

Three important patents<sup>84</sup> concern the production of pregnane derivatives from sapogenins. In the first R. B. Wagner claims the production of pregna-5:16-diene-2:3-diol-12:20-dione from  $\psi$ -kammogenin triacetate, and according to the second he obtains pregna-5:16-diene-2:3( $\beta$ )-diol-20-one diacetate from yuccagenin and lilagenin (via the isomeric  $\psi$ -yuccagenin). The third claims the production of progesterone from  $\psi$ -diogen-3-one by oxidation and hydrogenolysis, also from dibromokappogenin by a similar process, including debromination of the first product.

*Heart Poisons (Cardioactive Lactones).*—A study of the pharmacological properties of somalin has been made by R. Müller,<sup>85</sup> who states that it resembles digitoxin and digilanide A. This is of importance in view of the additional statement that the glycoside is readily obtained pure.

The work of Ruzicka's colleagues on the synthesis of steroid lactones related to the heart poisons has gone on during the year, with one outstanding contribution in the form of a ring-closure to form a butenolide ring by an intramolecular Reformatsky reaction. P. A. Plattner and H. Heusser,<sup>86</sup> using a simpler group in place of the steroid nucleus, have prepared benzyl bromoacetoxymethyl ketone and cyclised this to  $\beta$ -hydroxy- $\beta$ -benzylbutanolide by reaction with zinc; the product on dehydration yielded  $\beta$ -benzylbut- $\alpha$ ( $\beta$ )-enolide:



Three patents have been granted to R. C. Elderfield and his collaborators relating to the production of butenolides by the usual procedure, employing a Reformatsky reaction between ethyl bromoacetate and alkyloxymethyl ketones.<sup>87</sup>

<sup>83</sup> *J.C.S.*, 1945, 536; *A.*, 1945, II, 366.

<sup>84</sup> Parke, Davis & Co., U.S.P. 2,380,483-4, 2,383,472; *Chem. Abs.*, 1945, 5049; 1946, 178.

<sup>85</sup> *Helv. Physiol. Pharm. Acta*, 1944, 2, 203; *A.*, 1944, III, 210.

<sup>86</sup> *Helv. Chim. Acta*, 1945, 28, 1044; *A.*, 1946, II, 271.

<sup>87</sup> E. Lilly & Co., U.S.P. 2,356,153, 2,359,096, 2,359,208; *Chem. Abs.*, 1945, 1175, 1883.



## SYNTHETIC ŒSTROGENS.

A. L. Wilds and W. R. Biggerstaff<sup>88</sup> have modified the original Dodds-Robinson synthesis of stilbœstrol by preparing  $\alpha$ -ethyldeoxyanisoin from  $\alpha$ -*p*-anisylbutyric acid and anisole. W. Hoehn and H. E. Ungnade<sup>89</sup> and H. E. Ungnade and A. Ludutsky<sup>90</sup> have studied the hydrogenation of stilbœstrol, while H. von Euler and E. Adler<sup>91</sup> have studied its dehydrogenation with lead tetra-acetate. These latter claim a 73% yield of 4 : 4'-dihydroxydiphenylhexadiene and have also obtained  $\alpha\beta$ -diethylstilbenequinone, which has incomplete activity in 10- $\mu$ g. doses in the Allen-Doisy test on rats.

The preparation of the monoalkyl ethers of hexœstrol by treatment of hexœstrol with alkyl halide and alkali is dealt with in two patents by E. E. Reid<sup>92</sup> and F. C. Schmelkes,<sup>93</sup> and a third, granted to H. Medick,<sup>94</sup> claims the preparation of water-soluble acid esters of "hexœstrol," "stilbœstrol," and "dienœstrol" by treatment with a carboxylic acid sulphonyl halide.

A. H. Stuart, A. J. Shukis, and R. C. Tallmann<sup>95</sup> have prepared and biologically tested various  $\alpha\beta$ - and  $\alpha\gamma$ -dialkyl derivatives of  $\alpha\gamma$ -di-(*p*-hydroxyphenyl)propane.

An interesting dihydronaphthalene derivative, bearing structural relationship with hexœstrol and with œstradiol, has been made by C. Mentzer and (Mlle.) G. Urbain.<sup>96</sup> They prepared  $\alpha$ -*p*-anisyl- $\gamma$ -*m*-anisylbutyronitrile, hydrolysed this, and cyclised the acid to 1-keto-6-methoxy-2-*p*-anisyl-1 : 2 : 3 : 4-tetrahydronaphthalene. This was then treated with magnesium methyl iodide and the dehydrated product demethylated to 6-hydroxy-2-*p*-hydroxyphenyl-1-methyl-3 : 4-dihydronaphthalene. High œstrogenic activity is claimed for this product; it would be interesting to prepare similarly the 1-ethyl derivative, thus approaching more closely to the structures of hexœstrol and œstradiol.

Two indene derivatives with œstrogenic activity similar to that of stilbœstrol have been prepared by E. Adler and B. Hagglund.<sup>97</sup> 6-Hydroxy-2-*p*-hydroxyphenyl-1-methyl-3-ethylindene was prepared by the action of boron fluoride on  $\gamma\delta$ -di-*p*-hydroxyphenylhexa- $\beta\delta$ -diene (dienœstrol) followed by treatment of the initial product with alkali. The diacetate of this indene derivative was partly isomerised by pyridine at 100° by interchange of ethyl and methyl groups.

<sup>88</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 789; *A.*, 1945, II, 317.

<sup>89</sup> *Ibid.*, 1617; *A.*, 1946, II, 81.

<sup>90</sup> *J. Org. Chem.*, 1945, **10**, 307; *A.*, 1946, II, 81.

<sup>91</sup> *The Svedberg (Mem. Vol.)*, 1944, 246; *A.*, 1945, II, 91.

<sup>92</sup> Wallace & Tiernan Products, Inc., U.S.P. 2,385,468; *Chem. Abs.*, 1946, 177.

<sup>93</sup> *Idem*, U.S.P. 2,385,472; *Chem. Abs.*, 1946, 176.

<sup>94</sup> Winthrop Chemical Co., U.S.P. 2,359,276; *Chem. Abs.*, 1945, 1965.

<sup>95</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 1475; *A.*, 1946, II, 79.

<sup>96</sup> *Bull. Soc. chim.*, 1943, [v], **10**, 353; *A.*, 1945, II, 318.

<sup>97</sup> *Arkiv Kemi, Min., Geol.*, 1945, **19**, A, No. 23; *A.*, 1945, II, 396.



A most instructive review of the synthetic oestrogens has been published by U. V. Solmssen.<sup>98</sup>

### AMINO-ACIDS.

$\beta$ -Alanine is of particular interest as an intermediate in the preparation of pantothenic acid. During the year a considerable number of publications on its synthesis have appeared or have been abstracted. S. R. Buc, J. H. Ford, and E. C. Wise<sup>99</sup> have obtained 39% yields of  $\beta$ -amino-propionitrile from acrylonitrile; the amino-nitrile was then hydrolysed to  $\beta$ -alanine hydrochloride and the base obtained by use of anion-exchange resins. Acrylonitrile has also been used as starting material by A. Galat,<sup>100</sup> who condensed the nitrile with phthalimide and hydrolysed the product to  $\beta$ -alanine hydrochloride, using lithium hydroxide to obtain the base. G. H. Carlson and C. N. Hotchkiss<sup>101</sup> have obtained  $\beta$ -alanine by the treatment of acrylonitrile with aqueous ammonia under pressure; they also claim<sup>102</sup> to produce  $\beta$ -alanine by interaction of salts of acrylic acid with aqueous ammonia and ammonium carbonate under pressure.

Two closely related patents<sup>103</sup> claim the production of  $\beta$ -alanine by the hydrogenation of potassium cyanoacetate in ammoniacal solution, using Raney nickel as catalyst. Another similar patent, in the name of G. H. Carlson,<sup>104</sup> concerns the hydrogenation of cyanoacetic acid in acetic acid solution. E. J. Lawson and H. C. Parke<sup>105</sup> claim the preparation of  $\beta$ -alanine from its salts by the addition of organic bases (*e.g.*, diethanolamine) to alcoholic solutions.

Leucenol (from the seeds of *Leucæna glauca*) is considered by R. Adams, S. J. Cristol, A. A. Anderson, and A. A. Albert<sup>106</sup> to be probably  $\beta$ -5-hydroxy-2-pyridonoalanine.

*Tryptophan*.—The synthesis from gramine has now been given in detail<sup>107</sup> by N. F. Albertson, S. Archer, and C. M. Suter, following the preliminary report mentioned last year. *dl*-Tryptophan has been obtained in 66% yields from indole, through direct condensation of gramine with ethyl acetamidomalonate, by E. E. Howe, A. J. Zambito, H. R. Snyder, and M. Tishler.<sup>108</sup> N. F. Albertson and B. F. Tullar<sup>109</sup> have found ethyl acetamidocyanoacetate more effective than the substituted malonate in the above synthesis and have obtained a yield of

<sup>98</sup> *Chem. Rev.*, 1945, 37, 481.

<sup>99</sup> *J. Amer. Chem. Soc.*, 1945, 67, 92; A., 1945, II, 186.

<sup>100</sup> *Ibid.*, 1414; A., 1946, II, 6.

<sup>101</sup> Lederle Laboratories, U.S.P. 2,377,401; *Chem. Abs.*, 1945, 4333.

<sup>102</sup> *Idem*, B.P. 561,013; B., 1945, II, 48.

<sup>103</sup> F. Hoffmann-La Roche & Co., B.P. 561,764; B., 1944, II, 247. Produits Roche Soc. Anon., Belg.P. 446,571; *Chem. Abs.*, 1945, 713.

<sup>104</sup> Lederle Laboratories, Inc., B.P. 557,849; B., 1944, II, 64.

<sup>105</sup> Parke, Davis & Co., U.S.P. 2,372,092; *Chem. Abs.*, 1945, 3309.

<sup>106</sup> *J. Amer. Chem. Soc.*, 1945, 67, 89; A., 1945, II, 213.

<sup>107</sup> *Ibid.*, 36; A., 1945, II, 207.

<sup>108</sup> *Ibid.*, 38; A., 1945, II, 207.

<sup>109</sup> *Ibid.*, 502; A., 1945, II, 224.



71% from indole. J. Elks, D. F. Elliott, and B. A. Hems<sup>110</sup> have also contributed to the subject by obtaining a high yield of indole-3-aldehyde by hydrolysis of the decarboxylated anil of indole-3-glyoxylic acid.

E. T. Stiller<sup>111</sup> claims a full process for obtaining *dl*-tryptophan in improved yield from *o*-nitrotoluene. The nitro-compound is condensed with ethyl oxalate, treated with ferrous sulphate and ammonia, and esterified to ethyl indole-2-carboxylate. This is treated in the usual manner with zinc cyanide in presence of hydrogen chloride to give a 93—94% yield of ethyl indole-3-aldehyde-2-carboxylate. The anil of this is decarboxylated to indole-3-aldehyde and the azlactone, from the aldehyde with hippuric acid, then hydrogenated to benzoyl-*dl*-tryptophan (89% yield).

*Methionine*.—N. F. Albertson and B. F. Tullar<sup>109</sup> have also prepared *dl*-methionine by their new general method using ethyl acetamidocyanoacetate. They methylated monothioethylene glycol, obtaining  $\beta$ -methylthioethanol, which was chlorinated and condensed with the substituted cyanoacetate and the product hydrolysed to *dl*-methionine (38% overall). J. E. Livak, E. C. Britton, J. C. Vander Weele, and M. F. Murray<sup>112</sup> criticise the above method and also that of Booth, Burnop, and Jones (reported last year) on the grounds that the strong vesicant methyl  $\beta$ -chloroethyl sulphide is an intermediate. They prefer to brominate and then aminate butyrolactone to  $\alpha$ -amino- $\gamma$ -hydroxybutyric acid, which is then condensed with potassium cyanate to give  $\alpha$ -ureido- $\gamma$ -hydroxybutyric acid. This with hydrobromic acid gives 5-( $\beta$ -bromoethyl)hydantoin, which is converted into 5-( $\beta$ -methylthioethyl)hydantoin and hydrolysed to *dl*-methionine.

*Ornithine*.—N. F. Albertson and S. Archer<sup>113</sup> have employed their general ethyl acetamidomalonate method; acrylonitrile was condensed with the substituted malonate and the product hydrogenated to ethyl 3-acetamido-2-piperidone-3-carboxylate; this was then hydrolysed to *dl*-ornithine (overall yield 83%).

*Histidine*.—N. F. Albertson and B. F. Tullar<sup>109</sup> have prepared histidine among the various amino-acids obtained by the use of ethyl acetamidocyanoacetate. 4-Chloromethylglyoxaline hydrochloride gave a 66% yield of ethyl  $\alpha$ -acetamido- $\alpha$ -cyano- $\beta$ -gloxalanylpropionate, which on hydrolysis yielded 61% of *dl*-histidine (overall yield 18% from cane sugar). Using the older method, with ethyl acetamidomalonate, N. F. Albertson and S. Archer<sup>114</sup> obtained a 16% yield from fructose.

*Sulphonamides and Sulphones*.—The usual large number of papers describing new sulphonamide derivatives has appeared during the year;

<sup>110</sup> *J.C.S.*, 1944, 629; *A.*, 1945, II, 97.

<sup>111</sup> U.S.P. 2,380,479; *Chem. Abs.*, 1946, 367.

<sup>112</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 2218; *A.*, 1946, II, 306.

<sup>113</sup> *Ibid.*, 2043; *A.*, 1946, II, 179.

<sup>114</sup> *Ibid.*, 308; *A.*, 1945, II, 224.



probably the majority of these will remain of academic interest only. The patent literature on the subject is also extensive. A useful contribution comes from H. T. Openshaw and F. S. Spring,<sup>115</sup> who describe the separation of sulphonamides from sulphonalkylamides by acetylation and extraction of the sulphonacetamide with sodium bicarbonate solution.

M. A. Phillips<sup>116</sup> has obtained succinylsulphathiazole in 85% yield by interaction of the amino-compound with succinic acid or anhydride at 200°. The preparation of 2-aminothiazole and of sulphathiazole has been described by I. J. Postovski, V. I. Hmelevski, and N. P. Bedniagina.<sup>117</sup> 2-Aminothiazole was prepared in 67—84% yield by condensation of dichlorodiethyl ether with thiourea; in 70—80% yield from a fraction of the products of chlorination of ethanol (assumed to be monochloroacetaldehyde); in 80% yield from crude  $\beta$ -chloroacetal; in 72% yield from  $\alpha\beta$ -dichloroethyl isoamyl ether, and in 80% yield from chlorinated vinyl butyl ether. A 70% yield of acetylsulphathiazole was obtained by condensing the base with *p*-acetamidobenzenesulphonyl chloride, and removal of the acetyl group was effected by heating with alkali solution containing sodium chloride. The yield of hexahydrate of the sodium salt was 50% on the aminothiazole.

F. L. Rose and G. Swain<sup>118</sup> have described a novel preparation of a series of sulphanilamide derivatives of pyrimidine. This paper gives details of a route described by E. Haworth and F. L. Rose<sup>119</sup> in which 4-amino- or 4-acetamido-sulphonylguanidine is caused to react with  $\beta$ -diketones or  $\beta$ -ketocarboxylic esters.

A study of derivatives of *pp'*-diaminodiphenyl sulphone as antimalarials have been commenced at Harvard University; the first two papers,<sup>120</sup> by H. Heymann with L. F. Fieser, and H. Heymann with C. Heidelberger, have indicated promising activity in *pp'*-bismethylaminodiphenyl sulphone and in the corresponding bisformylamino-derivatives.

According to E. Biocca,<sup>121</sup> 4-nitrophenyl 4'-formamidophenyl sulphone is about seven times as potent as sulphathiazole against experimental toxoplasmosis in mice and in infections with pneumococcus type II; the toxicity is low. T. A. Henry and W. H. Grey<sup>122</sup> have described a simplified preparation of water-soluble derivatives of 4:4'-diaminodiphenyl sulphone previously described<sup>123</sup>; the sulphone is condensed with an aldehyde in the presence of sulphurous acid or a sulphite.

<sup>115</sup> *J.C.S.*, 1945, 234; *A.*, 1945, II, 230.

<sup>116</sup> *Chem. and Ind.*, 1945, 247; *A.*, 1945, II, 304.

<sup>117</sup> *J. Appl. Chem. Russ.*, 1944, 17, 65; *A.*, 1945, II, 259.

<sup>118</sup> *J.C.S.*, 1945, 689; *A.*, 1946, II, 51.

<sup>119</sup> With Imperial Chemical Industries Ltd., B.P. 552,887; *B.*, 1943, III, 193.

<sup>120</sup> *J. Amer. Chem. Soc.*, 1945, 67, 1979, 1986; *A.*, 1946, II, 196, 263.

<sup>121</sup> *Arquiv. biol. (Sao Paulo)*, 1943, 27, No. 255, 63; *Chem. Abs.*, 1945, 2133.

<sup>122</sup> Wellcome Foundation Ltd., B.P. 562,216; *B.*, 1944, III, 185.

<sup>123</sup> *Idem*, B.P. 491,265; *B.*, 1938, 1363.



## MISCELLANEOUS.

J. K. Cline, L. J. Berry, and T. D. Spies<sup>124</sup> report the isolation of a crystalline substance from liver extract, which may be necessary for the production of leucocytes in man. The substance contains nitrogen but no sulphur or phosphorus. One patient with macrocytic anæmia showed a positive hæmatological response to intramuscular injection of an impure preparation, but evaluation of its anti-anæmic properties requires isolation of larger quantities.

C. R. Harington and R. V. Pitt Rivers<sup>125</sup> have studied the conversion of di-iodotyrosine into thyroxine effected by von Mutzenbecher.<sup>126</sup> They have shown that atmospheric oxygen was essential and have made a further study of the effect of adding oxidising agents during incubation. They conclude that free iodine is probably the actual agent effective in bringing about this oxidation; the thyroxine obtained from *l*(+)-di-iodotyrosine has optical activity identical with that of the natural product.

Details of a synthesis of a norephedrine derivative by G. von Fodor<sup>127</sup> have become available during the year, though first published in 1943. *iso*Eugenol benzyl ether  $\psi$ -nitrosite was converted into  $\beta$ -nitro*isoeugenol* benzyl ether. Electrolytic reduction of this in acetic acid gave 32% of  $\beta$ -acetamido- $\alpha$ -hydroxy- $\alpha$ -(4-benzyloxy-3-methoxyphenyl)propane and 38% of  $\beta$ -(*N*-acetylhydroxylamino)- $\alpha$ -hydroxy- $\alpha$ -(4-benzyloxy-3-methoxyphenyl)propane. The former was hydrolysed to remove the acetyl group and debenzylated by hydrogenation to 4-hydroxy-3-methoxynorephedrine.

Pentamethylenetetrazole ("Cardiazole") has been obtained in 50% yield (of recrystallised material) from hydrazoic acid and *cyclohexanone* by N. M. Chapman, H. McCombie, and B. C. Saunders.<sup>128</sup>

The C.I.O.S. report on pharmaceuticals at the I.G. Farbenindustrie plant at Elberfeld<sup>77</sup> includes the preparation of 1-vinyl-2-pyrrolidone from butanediol by dehydrogenation to butyrolactone, treatment of the lactone with anhydrous ammonia, and vinylation of the resulting pyrrolidone with acetylene and alkali; a polymer of this is the essential constituent of Periston, used with apparent success as a substitute for blood plasma in the German army.

<sup>124</sup> *J. Amer. Chem. Soc.*, 1945, **67**, 2273; *A.*, 1946, III, 455.

<sup>125</sup> *Biochem. J.*, 1945, **39**, 157; *A.*, 1945, II, 360.

<sup>126</sup> *Z. physiol. Chem.*, 1939, **258**, 195; *A.*, 1939, II, 369.

<sup>127</sup> *Ber.*, 1943, **76**, [B], 1216; *Chem. Abs.*, 1945, 286.

<sup>128</sup> *J.C.S.*, 1945, 929; *A.*, 1946, II, 166.



# PHOTOGRAPHIC MATERIALS AND PROCESSES.

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AGAIN this past year has seen few outstanding advances in any branch of photographic processes or materials, which is understandable in view of the continued effect of war conditions on industry and research. Such advances are the culmination of research and development over a considerable period and thus, despite the cessation of hostilities, it is probable that it may be some time before the effect of this is felt.

On the other hand the number of patents taken out has been maintained, especially in the fields of colour photography and dye sensitisation. A noticeable trend in research as applied to photographic materials and processes has been the ever-increasing rôle of organic chemistry, not only in colour development and dye sensitisation, but also in the introduction of new classes of compounds capable of acting as emulsion sensitisers, stabilisers, anti-foggants, and blueing agents.

Work on various theoretical aspects has continued, particularly with regard to sensitivity and development; in connexion with the latter the series of papers by T. H. James is noteworthy.

## MANUFACTURE.

The production of spectrographic plates of substantially uniform contrast in the ultra-violet region of the spectrum has been described by E. P. Davey and M. D. Gauntlett.<sup>1</sup> Silver halide exerts very strong absorption in the region 2500—3100 Å., with the result that the image is confined largely to the surface of the plate. The usual increase of contrast found above this wave-length is due to the small absorption of the silver halide and greater penetration of the light into the emulsion layer. By incorporating in the emulsion layer a substance having a sufficient absorption in the near ultra-violet combined with the requisite transparency in the far ultra-violet the image is restricted to the surface also in the near ultra-violet, and a plate obtained giving substantially uniform contrast up to about 4000 Å.

An antihalation layer is formed according to S. E. Sheppard and R. C. Houck<sup>2</sup> by coating a gelatin solution at pH 7 containing alloxan, alloxantin, or triketohydrindene hydrate. The colourless layer thus formed on drying affords a coloured antihalation layer giving maximum absorption, which in the case of alloxan is coloured red with ash-free gelatin or orange with gelatin containing 1—2% of ash, and in the case of triketohydrindene hydrate reddish-purple.

<sup>1</sup> *J.S.C.I.*, 1945, 64, 70; C., 1945, 198.

<sup>2</sup> U.S.P. 2,184,024; B., 1944, II, 383.



The use of a polyvinyl acetal resin is suggested by R. J. Cox<sup>3</sup> for the preparation of waterproof sensitised photographic paper. This is made by coating both sides of the base with a hydrophobic solution of the resin Formvar 19-95 in ethyl alcohol-benzene to obtain a coating weight of 25-80 mg. per sq. dm. One side is further coated with a nitrocellulose-gelatin substratum followed by the gelatin-silver halide emulsion.

It is claimed that the generation of static charges during the coating of flexible supports of substances that are prone to such trouble is largely inhibited by applying to one or both selvedges prior to coating an electrically conducting border such as a layer of carbon dispersed in gelatin or cellulose ester.<sup>4</sup>

### COLOUR PHOTOGRAPHY.

Much more attention has been given to the subject of colour photography during the past year than to any other section of photography. However, practically the whole of the published work is concerned with two processes only. The first, which has claimed the most attention, is the multi-layer subtractive process, making use of colour development, whereby a dye is produced by the coupling action of a colour-coupler and the oxidation products of an amine developer. It is the quest after these colour-couplers which has occupied the bulk of the research work, and this report must, therefore, largely consist in a list of patents covering these coupling compounds.

To a much smaller degree attention has been given to the dye-bleach process of colour photography, and the name of B. Gaspar is again closely associated with the work. H. Wobbe<sup>5</sup> has described the Gaspar-color opaque material as consisting of an opaque white cellulose acetate support on to which is coated successively a red-sensitive emulsion layer containing a cyan azo-dye, a green-sensitive emulsion layer containing a magenta azo-dye, a yellow filter layer, and a blue-sensitive layer containing a yellow azo-dye; after exposure the dye image is obtained as a positive by the dye-bleach out process. B. Gaspar<sup>6</sup> has given the sensitisers and dyes which can be used for a dye-bleach-out colour material. For the red and green sensitisers pinacyanol and benzthio- $\psi$ -cyanine respectively are suggested. The dyes may be Diamine Pure Blue F<sub>1</sub>F (Schultz, "Farbstofftabellen," 7th Ed.), Sirius Ruben B (Ullmann, "Enzyklopädie der Technischen Chemie," Bd. IX, p. 524), magenta, and Xylenwalkgelb G. (Schultz), yellow. Non-diffusing dyes which can be used for the dye-bleach process are of the type  $(\cdot A \cdot \text{Aryl})_n$ , where A is a group that links the aryl radicals together, and  $n$  is an

<sup>3</sup> B.P. 568,782; B., 1945, II, 256; *Phot. Abs.*, 1945, 70.

<sup>4</sup> Kodak Ltd., and P. W. Tyler, B.P. 563,503; B., 1944, II, 383; *Phot. Abs.*, 1945, 3.

<sup>5</sup> *Camera (Baltimore)*, 67, 21; *Chem. Abs.*, 1945, 4013.

<sup>6</sup> Chromogen, Inc., U.S.P. 2,367,936; *Chem. Abs.*, 1945, 3489.



integer greater than 1, each of the groups A-Aryl carrying an azo-group in a side-chain with respect to the polymeric structure.<sup>7</sup>

As a variation of the dye-bleach process, diazo-compounds which couple with themselves on alkaline development are incorporated in gelatin layers in the material. Similarly amino-compounds are incorporated in the gelatin layers, and diazotisation and coupling can be carried out in the layers. In both cases the dyes formed must be such that are bleached *in situ* with developed silver.<sup>8</sup>

As a bleaching agent for the dye-bleach process an aqueous solution of an iminoaminomethanesulphinic acid, such as formamidinesulphinic acid, is recommended by Du Pont de Nemours & Co.<sup>9</sup>

A multi-layer material described by J. H. Coote and A. St. J. Austin<sup>10</sup> consists of a single silver halide emulsion layer coated with a colloid layer such as gelatin; in the silver halide layer one or two coloured images are produced. The colloid layer is then sensitised by dichromate, leuco-base, diazo-compound, or with silver salt; it is then processed to the appropriate colour to complete the two- or three-colour process. A multi-layer material in which each of the layers may be stripped has been prepared by J. G. Capstaff, G. F. Nadeau, and C. B. Starck<sup>11</sup> by separating the emulsion layers by a stripping layer or layers. Should there be more than two emulsion layers which are to be stripped independently, the stripping layers used are soluble in different solvents, namely, water-soluble layer consisting of cellulose ester of acyl content 13—19%, and spirit-soluble, water-insoluble stripping layer consisting of cellulose ester of acyl content 19—33%.

A high-iodide emulsion is used by E. B. Knott<sup>12</sup> to act as yellow filter for the multi-layer material processed by colour development, being either mixed with one of the emulsions, or itself acting as the blue-only-sensitive layer, or coated specifically as a separate filter layer.

W. R. Ruby and P. W. Vittum<sup>13</sup> have devised a method of preventing decomposition of unused colour-coupler by ultra-violet light, leading to degradation of the colour, by coating over the finished picture an ultra-violet filter consisting of such compounds as oxacyanines, diacyl-aminostilbenes, æsculin, primuline, etc. Again, to prevent degradation due to unused yellow coupler recurring in the top layer, the yellow colour-coupler is omitted from that layer in manufacture, and the material is developed in a developer so loaded that the yellow dye is formed in the top layer only.<sup>14</sup>

<sup>7</sup> B. Gaspar, and Chromogen, Inc., U.S.P. 2,356,759; *Phot. Abs.*, 1945, 88.

<sup>8</sup> *Idem*, U.S.P. 2,368,463; *Phot. Abs.*, 1945, 85.

<sup>9</sup> B.P. 571,078; B., 1945, II, 404.

<sup>10</sup> B.P. 568,323; B., 1945, II, 232; *Phot. Abs.*, 1945, 86.

<sup>11</sup> Eastman Kodak Co., U.S.P. 2,367,665; *Chem. Abs.*, 1945, 3216.

<sup>12</sup> Kodak Ltd., B.P. 569,495; B., 1945, II, 400.

<sup>13</sup> Eastman Kodak Co., B.P. 565,929; B., 1945, II, 160.

<sup>14</sup> P. W. Vittum, and Eastman Kodak Co., U.S.P. 2,362,599; B.P. 571,344; B., 1945, II, 404; *Phot. Abs.*, 1945, 31; *Chem. Abs.*, 1945, 2705.



The composition and structure of the colour-couplers now described, a résumé of a selection of which follows, are becoming more and more diverse and complicated. Considering first those which are fundamentally phenolic in character, a type usually producing cyan dyes, there are the di- $\alpha$ -naphthols<sup>15</sup> and compounds containing two naphthol groups linked by sulphur.<sup>16</sup> Other substances in this group are compounds<sup>17</sup> resulting from the reaction between a 3:5-disubstituted aniline and a phenol carrying a sulphonyl or carboxyl chloride substituent *ortho* to hydroxyl. The aniline substituents may be substituted carbamyl, carboxylamido, sulphamyl, amino, sulpho, or halogen. The substituent of the substituted carbamyl group may be another molecule of the phenolic compound, producing a compound containing two colour-coupler units. Substantive groups may also be present. Bis-3:5-(4'-sulpho-1'-hydroxy-2'-naphtho-amido)benzoyloctadecylamine is one example of this type of compound. Analogous compounds are anilides of aromatic hydroxy-carboxylic or -sulphonic acids with (a) *o*- or *p*-diamines, where one of the amino-groups carries one or two alkyl substituents, one containing at least five carbon atoms, or (b) aromatic amines substituted by an alkyl or alkoxy group having 5 or more carbon atoms. Other phenolic compounds<sup>18</sup> are 4-*o*-hydroxy-benz- or -benzenesulphon-amidodiphenyl having at 4'  $RX \cdot CO \cdot NH$  or  $RX \cdot SO \cdot NH$ , where R is phenol linked to X in the *ortho* position to hydroxy; X is *o*-hydroxyphenyl, a hydrogenated ring system, or an alkyl chain of more than 5 carbon atoms; if X is *o*-hydroxyphenyl, a 3'-alkylamino-group (alkyl of 5 or more C) is also present. Phenolic compounds substituted with a radical of the benzoxazole, benzthiazole, or benziminazole series have also been claimed.<sup>19</sup> Three of the colour-couplers giving cyan dyes are 2:6-diamino-4-hydroxypyrimidine,<sup>20</sup> 2-acylamido-5-alkylphenols,<sup>21</sup> and derivatives of 2:6-diketo-4-iminopiperidine.<sup>22</sup>

As substances which produce magenta dyes, H. D. Porter and A. Weissberger<sup>23</sup> have described 5-imino-3-hydroxypyrazolone and its derivatives, prepared from phenylhydrazine, cyanoacetyl chloride, and alkali. Another colour-coupling group is  $R \cdot SO_2 \cdot NHR'$ , where one of R and R' is an alkylaryl group, and the other is a cyanoacetylaryl group.<sup>24</sup> P. Bruylants and P. L. J. R. Merckx<sup>25</sup> have treated ketonic compounds

<sup>15</sup> B. Gluck and Dufay Chromex Ltd., B.P. 566,772; B., 1945, II, 128; *Phot. Abs.*, 1945, 59.

<sup>16</sup> *Idem*, B.P. 567,224; B., 1945, II, 200; *Phot. Abs.*, 1945, 85.

<sup>17</sup> A. Fröhlich and W. Schneider, Assrs. to General Aniline & Film Corp., U.S.P. 2,357,394-5; *Phot. Abs.*, 1945, 30.

<sup>18</sup> *Idem*, U.S.P. 2,366,324; *Phot. Abs.*, 1945, 60.

<sup>19</sup> *Idem*, U.S.P. 2,373,281; *Chem. Abs.*, 1945, 3742.

<sup>20</sup> C. H. Allen and J. A. Van Allan, U.S.P. 2,355,691; *Phot. Abs.*, 1945, 30.

<sup>21</sup> P. W. Vittum, W. D. Peterson, and H. D. Porter, U.S.P. 2,364,675; *Phot. Abs.*, 1945, 83.

<sup>22</sup> I. F. Salminen, P. W. Vittum, and A. Weissberger, U.S.P. 2,376,192; *Phot. Abs.*, 1945, 84.

<sup>23</sup> Eastman Kodak Co., U.S.P. 2,367,523; *Phot. Abs.*, 1945, 84.

<sup>24</sup> P. W. Vittum, W. D. Peterson, H. D. Porter, and Eastman Kodak Co., U.S.P. 2,364,675; *Phot. Abs.*, 1945, 83.

<sup>25</sup> U.S.P. 2,375,344; *Phot. Abs.*, 1945, 84.



having reactive methylene groups with a hydrazide also containing such a group; they state that pyrazolone formation does not occur, but that a colour-coupler is formed having two methylene groups separated by a chain containing a  $\cdot\text{NH}\cdot\text{N}\cdot$  group. These couplers on development produce orange as well as magenta dyes. The *p*-alkylbenzamido-derivatives of cyanoacetyl coumarone, or acetylacetaminophenyl or cyanoacetyl-aryl compounds, have been described as magenta or yellow dye-forming compounds.<sup>26</sup> 1-Phenylpyrazolones rendered non-migratory by long-chain alkyl substituents in the 3-position give improved dyestuffs when the sulphonic acid radical, present to solubilise the colour-coupler, is linked to the phenyl ring via an alkylene or hydroxyalkylene radical, instead of directly to the benzene ring.<sup>27</sup> Compounds containing two reactive methylene groups linked by a sulphur atom, such as thiobis-(1-phenyl-3-methyl-5-pyrazolone) or thiobisacetoacetanilide, prepared by treating the parent compounds with sulphur chloride or thionyl chloride, have been patented by B. Gluck and Dufay Chromex Ltd.<sup>28</sup>

As an example of the colour-couplers giving yellow dyes on development are cyclopentanone- or cyclohexanone-2-carboxylanilides, which may be nuclear-substituted except at C<sub>(2)</sub>.<sup>29</sup> Other colour-formers producing yellow dyes are *p*-phenylenediamines with one amino substituted by an acylacetyl group and the other by a *p*-alkylbenzoyl group.<sup>30</sup> According to A. Fröhlich and W. Schneider<sup>31</sup> improved colour-couplers are  $\text{NRR}'\cdot\text{A}(\text{N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COY})_n$ , where R is H or alkyl, R' is long-chain alkyl, aralkyl, or aryl, A is an aromatic ring containing a solubilising group, Y is acyl, and *n* is 1 or 2. Interesting compounds prepared by P. W. Vittum, K. P. Griffin, and A. Weissberger<sup>32</sup> possess rings containing nitrogen which is linked to an acylacetyl group, e.g., acetoacetylpiperidide.

Miscellaneous colour-couplers include the 9-keto-2-hydroxy-, 2:9-dihydroxy-, and 2-hydroxy-fluorenes substituted at 3:4 by a fused benzene or furan ring<sup>33</sup>; the keto-compounds on colour development give grey, black, or brown images, whilst the others give green images. Also used as colour-couplers with primary amines or hydrazine compounds as developers are basic *N*-substituted or unsubstituted  $\alpha$ -naphthylamines carrying a blocking group in position 2 and

<sup>26</sup> I. F. Salminen, A. Weissberger, and Eastman Kodak Co., U.S.P. 2,359,332; *Phot. Abs.*, 1945, 60.

<sup>27</sup> W. Schneider, A. Fröhlich, W. Zeh, and General Aniline & Film Corp., U.S.P. 2,354,552; *Phot. Abs.*, 1945, 30.

<sup>28</sup> B.P. 566,520; B., 1945, II, 200; *Phot. Abs.*, 1945, 59.

<sup>29</sup> H. D. Murray, B. Gluck, and Dufay Chromex Ltd., B.P. 566,771; B., 1945, II, 128; *Phot. Abs.*, 1945, 59.

<sup>30</sup> B. Gluck, and Dufay Chromex Ltd., B.P. 566,880; B., 1945, II, 200; *Phot. Abs.*, 1945, 59.

<sup>31</sup> General Aniline & Film Corp., U.S.P. 2,376,679; *Phot. Abs.*, 1945, 84.

<sup>32</sup> Eastman Kodak Co., U.S.P. 2,378,266; *Chem. Abs.*, 1945, 3743.

<sup>33</sup> E. B. Knott, and Kodak Ltd., B.P. 569,089; B., 1945, II, 288; *Phot. Abs.*, 1945, 84.



capable of coupling group in position 4.<sup>34</sup> Similar to these are compounds  $\alpha$ - or  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH·CH<sub>2</sub>·X·NHY, where X is a hydrocarbon radical which forms a chain interrupted by a hetero atom and Y is acidyl (free from OH).<sup>35</sup>

Finally two improvements in colour processing should be mentioned. A. Weissberger and P. W. Vittum<sup>36</sup> suggest the use of dihydroxymaleic acid or an ester either in the material or in the developer to prevent stain arising from aërial oxidation of the developer, and P. W. Vittum<sup>37</sup> has devised a hardening bath consisting of an alum, an organic acid (acetic acid), and a buffer that is free from sulphite or other deleterious substance.

### SENSITISERS.

Judging from the amount of published literature considerable research has been carried out on this subject. Research on sensitisers is now being undertaken in India, but it is from Russia that quite a proportion of the information on the purely theoretical aspects of optical sensitisation has been obtained. For instance, O. D. Barteneva and J. N. Gorochevskii<sup>38</sup> have investigated the effect of temperature on the spectral distribution of sensitivity of photographic layers. They have found that the sensitivity  $S$  sq. cm. per erg is independent of temperature between 60° and 20° and is reduced by lowering the temperature to -60°. The temperature coefficient  $d \log_{10} S/dT$  (where  $T$  is the temperature) is 0.002—0.02. The long-wave boundary of the emulsion sensitivity is shifted to shorter waves on cooling and the sensitivity band due to sensitisers is narrowed down. The lower is the concentration of the sensitiser, the more pronounced is the narrowing of the band due to the sensitiser. The absorption band of erythrosin and pinaverdol in gelatin is narrower at 30° than at 20°, thus accounting for the temperature-dependence of sensitised materials. S. Soloviev<sup>39</sup> has shown the absorption spectra of several sensitising dyes in various concentrations in several liquid media, and the spectral sensitivity due to these sensitisers. He postulates that the band representing aggregation in the presence of small amounts of gelatin or agar is due to adsorption of dye by micelles of the lyophilic colloids. The extent of shift between the maximum for absorption of light by dye in solution and the maximum for sensitisation is believed not to be significant owing to the appearance of the band of aggregated dye on the silver halide grain.

Of the new types of sensitisers perhaps one of the most interesting is that described by L. G. S. Brooker and R. H. Sprague.<sup>40</sup> In this type

<sup>34</sup> D. W. Woodward, and E. I. Du Pont de Nemours & Co., U.S.P. 2,362,519; *Chem. Abs.*, 1945, 2704. B.P. 569,647; B., 1945, II, 328.

<sup>35</sup> E. I. Du Pont de Nemours & Co., B.P. 569,646; B., 1945, II, 328.

<sup>36</sup> Eastman Kodak Co., U.S.P. 2,356,486; *Phot. Abs.*, 1945, 60.

<sup>37</sup> *Idem*, B.P. 565,551; B., 1945, II, 68; *Phot. Abs.*, 1945, 85.

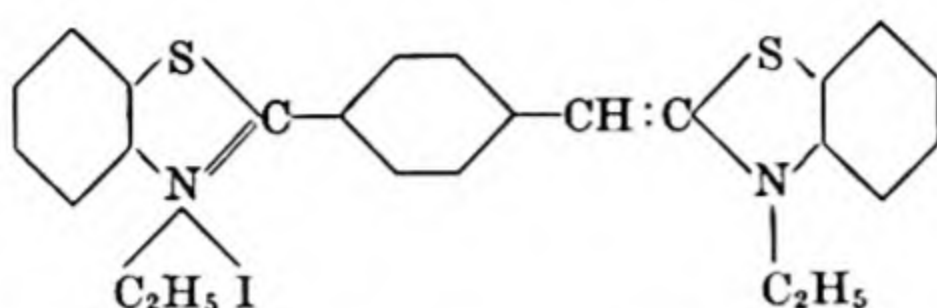
<sup>38</sup> *J. Tech. Phys. U.S.S.R.*, 1944, 14, 193; *Chem. Abs.*, 1945, 3214.

<sup>39</sup> *Acta Physicochim. U.R.S.S.*, 1944, 19, 592; A., 1945, I, 152.

<sup>40</sup> Eastman Kodak Co., U.S.P. 2,356,445; *Phot. Abs.*, 1945, 16.



four of the carbon atoms of a benzene ring form part of the methine chain joining the nitrogen atoms in a thiadicarbocyanine. Removing the elements of acid by means of ammonia from 2-(*p*-2'-benzthiazolyl-benzyl)benzthiazole diethiodide produces the dye of structure :



one of the type described. The sensitising maximum due to these dyes is displaced toward the short wave-lengths compared with ordinary dicarbocyanines.

Continuing investigations on thiazinocyanines, and now turning their attention to cyanines containing the 2:4-benzthiazine nucleus, B. Beilenson, F. M. Hamer, and R. J. Rathbone<sup>41</sup> have prepared the alkiodides of three alkylthio-2:4-benzthiazines and converted them into symmetrical and unsymmetrical cyanines, cyanine base, and mero-cyanines. Fusion of a mixture of a 3-alkylthiol-2:4-benzthiazine, a heterocyclic base with a reactive methyl group, and ethyl *p*-toluenesulphonate led to the formation of the cyanine base hydriodide in which the alkylidihydro-structure occurs in the nucleus other than benzthiazine. The dyes are strong sensitisers.

By treating brominated furyl or benzfuryl ketones with thioacetamide, 4-furyl- or 4-benzfuryl-2-methylthiazoles have been prepared. From the salts of these bases there have been obtained cyanines, carbocyanines, polycarbocyanines, etc., all sensitisers.<sup>42</sup> New styryl dyes are prepared by condensing heterocyclic bases having a reactive methyl  $\alpha$  to nitrogen with *o*- or *p*-hydroxybenzaldehydes which may be further substituted with halogen.<sup>43</sup> Unsymmetrical sensitisers containing a 2-methylindole nucleus are said by G. Wilmanns<sup>44</sup> to be sensitisers for silver chloride, chlorobromide, and chlorobromiodide emulsions, whilst emulsions sensitised with cyanine dyes, in which the negative radical is a sulphamate or an *N*-substituted sulphamate, are claimed to have superior blue-sensitivity.<sup>45</sup>

The normal methods for preparing thiazoles or selenazoles containing a condensed carbocyclic or heterocyclic system are based on the final thiazole ring formation from intermediates containing the other desired ring. E. B. Knott<sup>46</sup> has devised a method to give better yields in which the thiazole ring is first formed by a normal Hantzsch condensation

<sup>41</sup> *J.C.S.*, 1945, 222; *A.*, 1945, II, 261; *Phot. Abs.*, 1945, 71.

<sup>42</sup> E. I. Du Pont de Nemours & Co., B.P. 571,077; *B.*, 1945, II, 398.

<sup>43</sup> O. Reister, U.S.P. 2,320,654; *B.*, 1945, II, 199.

<sup>44</sup> General Aniline & Film Corp., U.S.P. 2,304,981; *B.*, 1944, II, 383.

<sup>45</sup> E. I. Du Pont de Nemours & Co., B.P. 566,684; *B.*, 1945, II, 128; *Phot. Abs.*, 1945, 46.

<sup>46</sup> *J.C.S.*, 1945, 455, 628; *A.*, 1945, II, 334, 418.



followed by an intramolecular cyclisation to a condensed system. For instance, the  $\beta$ -bromo-derivatives of  $\beta$ -benzoyl-propionic or -isobutyric acid condense with thioamides to give substituted 4-phenylthiazole-5-acetic acids; on cyclising with acetic anhydride derivatives of 4'-hydroxy-naphtha-1' : 2' : 4 : 5-thiazole are formed.

Useful intermediates for the preparation of chain-substituted carbocyanine dyes, certain 2-thioketonic derivatives of heterocyclic nitrogen bases can be prepared by treating the equivalent ketone derivatives with phosphorus pentasulphide in pyridine (e.g., 2-thioacetylmethylene-*N*-ethyldihydrobenzthiazole from acetylmethylene-*N*-ethyldihydrobenzthiazole).<sup>47</sup> In a similar manner by treating the 2-methine- $\omega$ -aldehyde derivatives of the heterocyclic nitrogen bases with phosphorus pentasulphide in benzene the thioaldehydes, intermediates for chain-unsubstituted carbocyanines, can be prepared.<sup>48</sup> P. de Smet and W. Mees<sup>49</sup> have devised a one-step method for preparing the above thioketonic derivatives from the 2-methyl quaternary salt of the heterocyclic nitrogen base which consists in treating this salt with the appropriate acyl chloride and phosphorus pentasulphide in pyridine.

More information regarding the supersensitising of combinations of dyes has been revealed. R. B. Collins and H. O. Dickenson<sup>50</sup> have found that carbocyanines substituted or unsubstituted in the central carbon atom of the trimethine chain have a supersensitising affect on dicarbocyanines which are 9-substituted or 9- and 12-substituted. F. M. Hamer and R. J. Rathbone<sup>51</sup> have described the preparation of chain-substituted dicarbocyanines using  $\beta$ -anilino- $\alpha$ -methylacraldehyde anil hydrochloride, prepared from  $\beta$ -bromo- $\alpha$ -methylacraldehyde diethyl acetal; these dyes, although powerful sensitisers, are not considered generally an improvement on the unsubstituted dicarbocyanine.

Quite a few non-sensitising compounds, when added to a dye-sensitised emulsion, increase the affect of the sensitising. B. H. Carroll and J. S. Spence have found that alkoxy- or hydroxy-aldehydes,<sup>52</sup> esters of quinoline- or pyridine-carboxylic acids,<sup>53</sup> and aromatic ketones, particularly those having an *o*- or *p*-alkoxy-substituent,<sup>54</sup> may supersensitise emulsions sensitised with a cyanine, carbocyanine, or merocyanine dye.

#### DESENSITISERS.

By condensing 3-nitroso-2-aryl-1-alkyl- or -1 : 2-diaryl-indoles with a quaternary salt of a heterocyclic compound containing reactive groups azadimethinecyanines are formed; these compounds incorporated in a

<sup>47</sup> L. G. S. Brooker, G. H. Keyes, and Kodak Ltd., B.P. 566,010; B., 1945, II, 73; *Phot. Abs.*, 1945, 16.

<sup>48</sup> K. Kumetani and O. Reister, U.S.P. 2,349,179; *Phot. Abs.*, 1945, 17.

<sup>49</sup> U.S.P. 2,356,509; *Phot. Abs.*, 1945, 18.

<sup>50</sup> B.P. 571,231; B., 1945, II, 398.

<sup>51</sup> *J.C.S.*, 1945, 595; A., 1945, II, 415.

<sup>52</sup> U.S.P. 2,355,630; *Phot. Abs.*, 1945, 17.

<sup>53</sup> U.S.P. 2,361,928; *Phot. Abs.*, 1945, 17.

<sup>54</sup> U.S.P. 2,373,659; *Chem. Abs.*, 1945, 4014.



photographic emulsion are strong densensitisers to visible light but have little effect on the X-ray sensitivity.<sup>55</sup>

### PHOTOGRAPHIC EMULSIONS.

Further work has been carried out on the use of certain synthetic resins in place of gelatin for the preparation of photographic silver halide emulsions. R. W. Berriman and E. P. Davey<sup>56</sup> have proposed the use for this purpose of a 9 : 1 mixture of polyvinyl acetate (71—95% acetate content) and polyvinyl alcohol. It is claimed that emulsions prepared with this binder can be coated without the use of any gelatin or other type of substratum. The incorporation of boron compounds, such as borax, sodium metaborate, or boric acid, in concentrations up to 5%, followed by fuming with ammonia or a primary amine is stated to induce setting in a polyvinyl alcohol emulsion,<sup>57</sup> whilst the use of a condensation product of formaldehyde and melamine is claimed to act as a hardener for a polyvinyl alcohol emulsion.<sup>58</sup> D. R. Swan<sup>59</sup> has suggested the inclusion in photographic emulsions of water-soluble polyvinyl acetals, in which at least part of the acetyl groups are 4-formyl-phenyltrialkylammonium salt acetal groups, as dispersing agents for silver halide.

According to W. J. Weyerts,<sup>60</sup> the sensitivity of a gelatino-silver halide emulsion is improved by the addition of 5—25% by weight of the gelatin of an ammonium, hydrazine, or alkali salt of benzoic acid, its amino-, hydroxyl, or halogen substitution product, or a benzenesulphonic acid or its amino- or halogen substitution product, a specific example being sodium metanilate. The same worker<sup>61</sup> claims for the same purpose the addition of 5—25 g. per litre of a water-soluble salt of an unsaturated lower aliphatic acid, such as acrylic, substituted acrylic, itaconic, citraconic, or maleic acid. A marked increase in the sensitivity of a silver halide emulsion has been found by C. Waller, R. B. Collins, and E. C. Dodd<sup>62</sup> to result from the addition of a small quantity of a soluble gold salt (of the order of 1—100 c.c. of a 1 in 10,000 solution per litre of emulsion) prior to or during the digestion period. It is stated that the pH of the emulsion is particularly important and should be maintained at a value below 8 during digestion and subsequent coating, a further increase of speed being obtained when the emulsion is kept on the acid side of neutrality. Any soluble gold salt may be used but sodium chloroaurate has been found to be particularly effective.

<sup>55</sup> R. C. Haworth, F. G. Mann, and Imperial Chemical Industries Ltd., B.P. 571,025; *J.C.S.*, 1944, 670; *B.*, 1945, II, 400; *A.*, 1945, II, 171; *Phot. Abs.*, 1945, 47.

<sup>56</sup> With Kodak Ltd., B.P. 564,267; *B.*, 1944, II, 383; *Phot. Abs.*, 1945, 15.

<sup>57</sup> W. G. Lowe and K. P. Griffin, U.S.P. 2,376,371; *Phot. Abs.*, 1945, 102.

<sup>58</sup> W. G. Lowe and W. F. Fowler, jun., B.P. 568,399; U.S.P. 2,276,323 and 2,286,215; *B.*, 1945, II, 255; *Phot. Abs.*, 1945, 94.

<sup>59</sup> U.S.P. 2,358,836; *Chem. Abs.*, 1945, 1363.

<sup>60</sup> U.S.P. 2,367,549; *Chem. Abs.*, 1945, 3217.

<sup>61</sup> W. J. Weyerts, U.S.P. 2,380,280; *Phot. Abs.*, 1945, 103.

<sup>62</sup> B.P. 570,393; *B.*, 1945, II, 355; *Phot. Abs.*, 1945, 103.



In the patent literature further claims have been made for the addition of particular compounds to photographic emulsions. Thiosalicylic acid when present in the emulsion in the proportion of 0.2—20 mg. per 50 g. of silver halide is stated to inhibit the formation of fog during development.<sup>63</sup> Antifoggants to be incorporated in the emulsion in the proportion of 1—15 g. per litre immediately prior to ripening are ethyl trichloroacetate and sodium *dl*-mandelate.<sup>64</sup> D. J. Fry and J. D. Brooks<sup>65</sup> have described compounds of the general formula  $R \cdot CO \cdot NH \cdot NH \cdot CS \cdot R'$ , where R is hydrocarbon and R' is amino or thiol, for inclusion in emulsions of the bromide or chloride type for the production of blue-black images.

Nitroaldehydes<sup>66</sup>  $R \cdot CH(NO_2)_x \cdot [CHX]_y \cdot [CH_2]_z \cdot CHO$ , where R is hydrogen or an alkyl group containing not more than 6 carbon atoms, and may be substituted, X is hydrogen, halogen, or hydroxyl and  $x$ ,  $y$ , and  $z$  are whole numbers less than six or may be zero, act as hardening agents that are free from either fogging or desensitising action in gelatino-silver halide emulsions.

The work of S. E. Sheppard<sup>67</sup> on the amphipathic character of gelatin is of particular interest with regard to the retention of gelatin by silver bromide in confirming the hypothesis of the presence of a unimolecular layer and the attachment of a second layer to this by weaker forces.

The spectral distribution of sensitivity in the region 2500—5500 Å. of a series of silver halide emulsions prepared by the same method but of differing composition has been determined by I. I. Breido and J. N. Gorochevskii.<sup>68</sup> It is considered that the change in absorption and sensitivity from pure silver bromide to silver iodobromide which is detectable at 1% silver iodide indicates that the silver iodide is present as a separate phase.

### THE THEORY AND TECHNIQUE OF DEVELOPMENT.

T. H. James<sup>69</sup> has contributed a series of papers on the charge effect in relation to the kinetics of photographic development. He postulates that the approach of the negatively charged developer ions to the surface of the grain is opposed by charge barriers originating both with the gelatin and with the adsorbed bromide ions. The neutral salt effect on the rate of development originates primarily from a depression of the gelatin charge barrier while a charge in the bromide barrier is mainly responsible for certain other kinetic effects such as induction period of development and the accelerating action of phenosafranine. Charge effects depending

<sup>63</sup> H. D. Russell, U.S.P. 2,377,375; *Phot. Abs.*, 1945, 93.

<sup>64</sup> G. E. Fallesen, U.S.P. 2,378,203-4; *Phot. Abs.*, 1945, 94.

<sup>65</sup> B.P. 571,174; B., 1945, II, 398.

<sup>66</sup> R. H. Zappert, U.S.P. 2,372,873; *Phot. Abs.*, 1945, 93.

<sup>67</sup> *Science*, 1944, 100, 545; *Phot. Abs.*, 1945, 93.

<sup>68</sup> *Acta Physicochim. U.R.S.S.*, 1944, 19, 104; B., 1945, II, 160; *Phot. Abs.*, 1945, 71.

<sup>69</sup> *J. Chem. Physics*, 1944, 12, 453; A., 1945, I, 142; *Phot. Abs.*, 1945, 95. *J. Franklin Inst.*, 1945, 240, 15, 83, 229; B., 1946, II, 67.



on the bromide barrier are found to be less pronounced when optically sensitised emulsions are used than when the corresponding unsensitised materials are employed. These kinetic effects originating in the action of the charge barrier can be divided into two groups, namely, those produced primarily by a general charge of magnitude of the barrier, and those resulting from a localised charge in the vicinity of the growing development specks. James finds the basic cause of the induction period to lie in localised decrease of the bromide potential barrier as development proceeds, which can operate even after development of the grain is discernible in the microscope if several development centres are involved. The abnormal behaviour of sulphite-free caustic quinol developers in the production of abnormally high gammas and short toe characteristics is attributed to a localised action of the oxidation product of the developer on the bromide barrier increasing the local reduction rate.

Studying the action of formaldehyde-quinol developers, J. A. C. Yule<sup>70</sup> has concluded that activation of this developer is caused by oxidation products of development. The activated developer diffusing out from an exposed area does not cause development of unexposed grains, but greatly accelerates development of slightly exposed grains. The main function of the formaldehyde is that of a sulphite buffer controlling the concentration of free sulphite ions and hence the rate of removal of free sulphite ions. A quinol developer containing only 1 g. of sodium sulphite per litre was found to give the same development characteristics as the formaldehyde-quinol developer. According to T. H. James<sup>71</sup> the fogging action of a quinol developer increases with increasing sulphite concentration to a region in which fog formation is practically independent of sulphite concentration, and finally again increases at high concentrations. The same author<sup>72</sup> has determined maximum emulsion speeds and gammas obtainable with a series of developing agents, development being carried out in an inert atmosphere and in the absence of sulphite, thus confining it to the surface latent image. Since seven of the eleven agents tested gave substantially the same values, the critical size and configuration of the latent image centre that will just promote development must be substantially the same for each of these agents. The other four agents gave lower values, no agent or combination of agents being found that would give higher speed values.

J. Pouradier and M. Abribat<sup>73</sup> have suggested that any oxidation-reduction system with a real or apparent potential of less than 0.120 v. is capable of acting as a developer without regard to the structure of the developing agent. Certain systems with normal potentials greater than

<sup>70</sup> *J. Franklin Inst.*, 1945, 239, 221; *B.*, 1945, II, 396; *Phot. Abs.*, 1945, 64.

<sup>71</sup> *J. Phot. Soc. Amer.*, 1944, 10, 271; *Phot. Abs.*, 1945, 96.

<sup>72</sup> T. H. James, *J. Franklin Inst.*, 1945, 239, 41; *B.*, 1946, II, 28; *Phot. Abs.*, 1945, 95.

<sup>73</sup> *Sci. Ind. Phot.*, 1944, 15, 204; *Chem. Abs.*, 1945, 4553.



0.120 v. can act as developers where conditions are such that the oxidised form is eliminated by destruction or by complex formation. Depth development is given by a diaminophenol solution of pH 3.6 containing sodium bisulphite and sodium sulphite. The potential at this pH being greater than 0.120 v., no development takes place until penetration into the gelatin has caused the pH to rise and the redox potential to fall to below 0.120 v.

Addition of cationic surface-active agents to the developer<sup>74</sup> has been found to cause increased developability of the least exposed parts of an emulsion, and thus give rise to an increase in speed; the effect, however, is not shown with developers of the *p*-phenylenediamine class. It is claimed that the addition of thiocyanate<sup>75</sup> together with an ethanolamine to developers for silver halide emulsions having a polyvinyl resin binder reduces the time of development, increases contrast, and diminishes opalescence.

The Schwarzschild exponent for a large number of commercial development papers has been determined by H. Bäckström and H. Gordon<sup>76</sup> by comparison of results obtained by wedge exposures at 5 and 60 seconds and using D.I.N. standard metol-quinol developer. The exponent was found to vary between 0.76 and 1.08. The influence of development was also studied, the same ultimate value of the exponent being obtained for all the ordinary types of developer investigated. For short development times, however, the value varied considerably with the developer used.

L. A. Jones and G. C. Higgins<sup>77</sup> have attempted to determine the relationship between granularity and graininess of developed photographic materials. Granularity refers to the spectral variations in transmitting characteristics, whilst graininess refers to the visual appearance of the granular structure of the developed photographic material. None of the several methods proposed by various workers used for measuring granularity was found to give the same functional relation between granularity and the density of the silver image as that existing between graininess and density. By the arbitrary choice of a density level, which is not the same for all of the methods, it is possible for all these methods to give granularity values which place the different photographic materials in approximately the same order as the graininess values. Even where the order is the same, however, granularity values are not proportional to the graininess values. The conclusion is reached that the methods of determination of granularity used measure one or more, but not all, the factors which determine graininess.

<sup>74</sup> D. J. T. Howe and J. W. Glassett, B.P. 566,314; B., 1945, II, 92; *Phot. Abs.*, 1945, 95.

<sup>75</sup> G. T. Eaton and J. I. Crabtree, B.P. 565,135; B., 1945, II, 39; *Phot. Abs.*, 1945, 4.

<sup>76</sup> *Ing. Vetenskaps-Akad. Handl.*, 1944, No. 176; *Chem. Abs.*, 1945, 32.

<sup>77</sup> *J. Opt. Soc. Amer.*, 1945, 35, 435; B., 1946, II, 68; *Phot. Abs.*, 1945, 105.



## LATENT IMAGE AND THEORY OF SENSITIVITY.

As a result of the analysis of several hundred characteristic curves for a variety of photographic emulsions under widely differing development conditions, L. Silberstein and A. P. H. Trivelli<sup>78</sup> have concluded that the measured densities for the total range of exposures applied can be represented by functions of the exposure derived rigorously from the quantum theory under the assumption of a simple schematic form of grain size frequency distribution in the emulsion and implying in most cases only the first, second, or third lowest values of the quantum number  $r$ . By application of this quantum theory of exposure<sup>79</sup> to pure silver bromide emulsions it has been demonstrated that the use of the first derivatives of the fog-corrected characteristic curves makes it possible to study the sensitivity distribution among the grains of an emulsion. These fog-corrected characteristic curves can be rotationally symmetrical or asymmetrical and both types can be represented by equations which require single probability distributions of sensitivity among the grains. With a silver bromide emulsion sensitised by a sulphur-containing sensitiser it is found, however, that the first derivative of the characteristic curve becomes irregularly asymmetrical; this cannot be explained by a change of the parameters of the distribution of sensitivity among the grains, but it is possible to analyse such a curve quantitatively into two simple curves. For a given emulsion it is further found that the type of curve obtained can be dependent on the development.

It has previously been stated by H. Arens, J. Eggert, and F. G. Kleinschrod that the red-green-sensitivity of an unsensitised silver halide emulsion was produced by a change of the surface properties on the grain. They now support this interpretation<sup>80</sup> by the artificial production of colloidal silver at the grain surface. They found, however, no shift in sensitivity of a pure silver chloride or bromide emulsion by pre-exposure, or by the addition of colloidal silver however this was produced. It was necessary for sufficiently intimate contact to be obtained that the two components be precipitated together as prescribed by Lüppo-Cramer. Increase in red-green-sensitivity was shown by mixed emulsions prepared in this manner as the percentage of colloidal silver was increased; above a certain amount, however, of colloidal silver complete fogging took place.

P. V. Meiklyar,<sup>81</sup> studying the photographic additivity of light action of various spectral compositions, has concluded that van Kreveld's equation for the calculation of the sensitivity to mixed irradiation from the sensitivities to single wave-lengths is valid only when the relation between the optical density and light energy is identical over the range of wave-lengths studied.

<sup>78</sup> *J. Opt. Soc. Amer.*, 1945, **35**, 93; *B.*, 1945, **II**, 288.

<sup>79</sup> A. P. H. Trivelli, *J. Franklin Inst.*, 1945, **239**, 101; *Phot. Abs.*, 1945, 72.

<sup>80</sup> *Z. wiss. Phot.*, 1943, **42**, 33; *Chem. Zentr.*, 1944, **I**, 512.

<sup>81</sup> *J. Tech. Phys. U.S.S.R.*, 1944, **14**, 216; *Chem. Abs.*, 1945, 3214.



Jahr's experiments on the effect of the magnetic field on the photographic plate have recently been repeated by E. Cotton.<sup>82</sup> With modern photographic plates it was found that the magnetic field was without effect, but a repetition of the original experiment using old Lumière plates and a pyrogallol developer gave a blackening which was most pronounced between the poles of the magnet. The author explains this by the experimental conditions which gave rise to an increased layer of developer which was further protected from aërial oxidation in the region of the magnetic pole.

It has been observed that a smaller developable density is obtained when exposure takes place in the presence of a heavy static pressure. H. Bäckström, C. A. Bruno, and M. Müller<sup>83</sup> explain this in terms of the Gurney-Mott theory of latent image formation. It is known that pressure causes a decrease in the conductivity of silver chloride and silver bromide, and thus in the emulsion grains the rate of migration of silver ions to the sensitivity speck is reduced by the application of higher pressure, thereby decreasing the efficiency of formation of development centres. Experimental confirmation of this effect of pressure was obtained, the general results obtained being interpreted as showing that the reason for the inefficiency of the exposure under pressure lies in the relative instability of the latent image nuclei in the early stages of their formation.

It has been found that the vapours of certain organic acids, such as formic, acetic, or propionic, and of volatile weak inorganic acids, such as sulphurous acid, are capable of intensifying the latent image.<sup>84</sup> This effect occurs only when the vapour of the acid or a solution in a non-polar solvent, such as benzene, is brought in contact with the photographic emulsion after exposure. Similar treatment prior to exposure gives rise to desensitisation. High-speed emulsions are the more responsive and many show an increase in speed up to threefold. Although minute quantities of water vapour are stated to be necessary for the process, aqueous solutions themselves of the acids cause desensitisation.

#### FINISHING.

It would appear that few outstanding advances have been made relating to this branch of the photographic process. Belated news comes of a concentrated stock fixing syrup which is stable between 6° and 49°<sup>85</sup>; this consists of a soluble thiosulphate, alum, and a sulphite optionally with a hydrotropic substance (urea). Another stock dry fixing-hardening composition consists of an acid sulphate, sodium thiosulphate, sodium sulphite, sodium acetate, and alum.<sup>86</sup> C. S.

<sup>82</sup> *Ann. Physique*, 1944, [xi], **19**, 215; B., 1945, II, 255.

<sup>83</sup> *The Svedberg (Mem. Vol.)*, 1944, 65; A., 1945, I, 72; *Phot. Abs.*, 1945, 105.

<sup>84</sup> F. W. H. Mueller and J. E. Bates, *J. Phot. Soc. Amer.*, 1944, **10**, 586; *Chem. Abs.*, 1945, 3213.

<sup>85</sup> G. P. Ham, and Amer. Cyanamid Co., U.S.P. 2,311,293; B., 1944, II, 383.

<sup>86</sup> H. D. Russell, L. E. Muehler, and Eastman Kodak Co., U.S.P. 2,378,248; *Chem. Abs.*, 1945, 3748.



Hollander<sup>87</sup> has revealed that an approximately 1% solution of a basic chromium sulphate, of basicity about 30—55% (pH 3.3—3.9), when employed between development and fixing causes permanent hardening with no reticulation, yet without causing the gelatin to become brittle; at the same time the rate of drying is increased. Another type of hardening agent, described by C. J. Staud and C. S. Potter,<sup>88</sup> is a dialkyl diketone (*e.g.*, diacetyl, dichlorodiacetyl, diacetylacetone, etc.) used in the processing solution in concentrations between 0.15 and 1.5% by weight of the solution. To facilitate development in normal developers under high-temperature conditions, the material to be developed can be first hardened in a bath containing formaldehyde to insolubilise the gelatin, sodium sulphate to retard swelling, and as antifoggant and restrainer 6-nitrobenziminazole nitrate.<sup>89</sup> A combined developing and fixing bath, consisting of the normal developing and fixing agents activated by triethanolamine, is the subject of a patent by J. N. Boberg.<sup>90</sup>

Intensification by means of sulphur dioxide gas is described by N. L. Simmons, whilst H. A. Miller and J. I. Crabtree<sup>92</sup> have shown that undesirable warm tones with chromium intensifiers can be eliminated by adding very small quantity of benztriazole derivatives to the re-developer. P. Fripp<sup>93</sup> has devised a method of controlled reduction. The negative is first treated in a bath of potassium permanganate acidified with hydrochloric acid until the bleaching has progressed to the desired extent, followed by a bath of potassium permanganate acidified with sulphuric acid to remove silver; the silver chloride is then redeveloped.

There are a few developments concerned with toning processes. A barium sulphide toned image of colder tone is obtained by increasing the potassium bromide content of the ferricyanide reducing agent used; by diluting the barium sulphide solution or by adding thiourea a more yellow result is obtained.<sup>94</sup> E. T. Howell<sup>95</sup> has described how the tones of sulphide-toned papers can be modified by partial redevelopment in a weak metol-quinol developer and complete development in a sulphide bath, or by bleaching in a ferricyanide-mercuric chloride bath of varying proportions and redeveloping in a sulphide bath. Lead toning in a solution of thiosulphate and a lead salt is said to improve poor sulphide tones.<sup>96</sup>

To discharge the colour from scrap film containing dye, ozone is passed into an aqueous suspension of pH less than 7.<sup>97</sup>

<sup>87</sup> Röhm & Haas Co., U.S.P. 2,359,217; *Phot. Abs.*, 1945, 35.

<sup>88</sup> Eastman Kodak Co., U.S.P. 2,356,477; *Phot. Abs.*, 1945, 35.

<sup>89</sup> H. A. Miller, J. I. Crabtree, and H. D. Russell, *J. Phot. Soc. Amer.*, 1944, 10, 397, 453; *Chem. Abs.*, 1945, 31.

<sup>90</sup> B.P. 571,389; *B.*, 1945, II, 402.

<sup>91</sup> Eastman Kodak Co., B.P. 570,703; *B.*, 1945, II, 356.

<sup>92</sup> *J. Phot. Soc. Amer.*, 1943, 9, 300; *Phot. Abs.*, 1945, 5.

<sup>93</sup> *Brit. J. Phot.*, 1944, 91, 433.

<sup>94</sup> H. Cuisinier, *Photographie*, 1943, 117; *Chem. Abs.*, 1944, 5736.

<sup>95</sup> *J. Phot. Soc. Amer.*, 1945, 11, 12, 113; *Chem. Abs.*, 1945, 3215.

<sup>96</sup> *Ibid.*, 1944, 10, 12; *Chem. Abs.*, 1944, 6217.

<sup>97</sup> H. T. Clarke, J. G. Stamfi, and Eastman Kodak Co., U.S.P. 2,364,343; *Phot. Abs.*, 1945, 64.



# SANITATION AND WATER PURIFICATION.

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DURING the year 1945, details have been published of much noteworthy research. Besides its purely scientific interest, a great deal of the work has the added importance of offering prospects of improving works practice. Particulars are now being given of work which had to be kept secret during the war, and so we can expect further interesting disclosures in the near future.

One of the main objects of such a report as this is that of tracing trends of opinion and development, as distinct from noting in detail every individual publication on the subjects under review; indeed, the latter is a task impossible of fulfilment. One factor which is likely to influence policy and operation is the growing realisation of the community of interest between the two main services dealt with in this Report—namely, water supply and sewage disposal. Of course, it has long been recognised that the two subjects had much in common, but it is probable that insufficient effort has been made to apply discoveries in one field to problems in the other. While it would be ridiculous to hold that the two services take no note of each others' developments, it is nevertheless remarkable that there is not closer liason, in view of the fact that the purification of water and sewage have so many processes in common. For instance, although there are naturally differences in detail and in degree, such operations as flocculation, sedimentation, and filtration are common to both services, while there is little doubt that in matters of engineering design each could have learned more from the other. Probably this lack of full co-operation has been due to the subconscious feeling that sewage and water are so different—the one so dirty and the other so clean—that the problems of their purification are widely different. In fact, many of the differences are of degree, rather than kind. This point is being emphasised by the increasing use of river water for public and industrial water supplies. This tendency is likely to become more marked in the future, for it seems certain that the volume of water needed for public supplies will increase. The policy of providing piped supplies to rural areas will place a further load on water undertakings.

As a result of this combination of circumstances, consideration will therefore have to be increasingly given to the abstraction of water from the lower reaches of rivers. In other words, streams containing sewage works effluents from towns upstream are likely to come into growing use for water supplies downstream. No doubt this trend is partly responsible for the more general realisation of the inter-relation between sewage disposal and water supply, leading in turn to recognition of the fact that



processes evolved in one service are often worth exploring for possibilities of usefulness in the other. The use of a filter of the sewage works type for the preliminary treatment of a supply from an impure river is an illustration of this.

#### WATER SUPPLY.

It is pleasing to be able to report that the water undertakings of this country are showing a more active interest in research. This was badly needed, and will undoubtedly bring improvements in both efficiency and economy. The improved attitude towards research has not yet made any great impact on the technical literature, although some noteworthy contributions have been made. However, there is evidence that undertakings which have in the past neglected the scientific side of their work are now ready to remedy this defect.

Various aspects of chlorination continue to provide fruitful topics for research and argument, both in this country and in America, while the search for methods for purifying raw waters of poor quality (some of which would have been regarded as hopelessly polluted a generation ago) has been the motive for some interesting work.

In the field of administration the outstanding event of the year was the passing of the Water Bill, which was designed to give effect to the policy set out in a White Paper<sup>1</sup> during the previous year. The new legislation is noteworthy in that it places for the first time on the Ministry of Health the "specific duty of promoting in England and Wales the provision of adequate water supplies, the conservation of water resources and the effective execution by water undertakers, under his control and direction, of a national water policy."

It is interesting to compare the terms of the Bill with the recommendations of the British Water Works Association Post-War Planning Committee,<sup>2</sup> as set out in their second report on the control of water resources. This body recognised the need for co-ordination and planning on a national scale, as provided in the Bill. However, in preference to attaching powers to an existing minister, they advocated the appointment of a Minister of Water, having responsibility for matters outside the normal sphere of water supply. Their suggestion was that the Minister of Water should be responsible for the conservation and utilisation of the water resources of the country and should be answerable in Parliament for all water interests, including public water supplies, prevention of pollution, land drainage, fresh-water fisheries, and water supplies for agriculture, inland navigation, and power.

When a joint meeting of the Geological Society and the Institution of Water Engineers<sup>3</sup> discussed "Water in relation to town and country planning" much useful information and some interesting suggestions came to light. For example, H. P. Hill said that a substantial proportion

<sup>1</sup> "A National Water Policy," *Cmd.* 6515.

<sup>2</sup> *J. Brit. Water Works Assoc.*, 1944, 26, 92.

<sup>3</sup> *Nature*, 1944, 154, 171.



of the head waters of the rivers rising in the Pennines had been impounded long ago to supply canals which were now disused; some of this water might be used for public supply. W. S. Boulton said mine water was widely used to supply canals in the Midlands, but it had proved too corrosive for use in the cooling towers in electricity generating stations. He suggested that effluents from sewage works might be used for the latter purpose. It may be noted that, in effect, this practice is already followed in a few cases.

### *Coagulation and Flocculation.*

As it becomes necessary to make increasing use of raw waters of lower quality, coagulation and flocculation become more important in water treatment. Their investigation, coupled with that of sedimentation, should provide opportunities for much useful research, both in the laboratory and on the plant. Furthermore, this field of work is one in which a close comparison of the researches and methods employed in the purification of water and sewage, respectively, is well worth while, for the problems and principles prevailing in the two services have many points in common.

R. E. Noreus<sup>4</sup> has described a method for using activated silica to coagulate a highly coloured water. Activated silica was prepared by adding ammonium sulphate to a solution of sodium silicate containing 1.75% of silica. The mixture was aged for two hours to allow the micelles to grow, and was then diluted to 1.3% of silica to prevent further growth. The silica (5—12 p.p.m.), together with alum, was added to river water flowing through an Accelator. The effect of the activated silica was to reduce the colour and the turbidity of the filtered water and to increase the capacity of the Accelator from 2000 to 4000 gals. per min. However, a fall in temperature to about 0° caused the colour and turbidity of the filtered water to increase, in spite of increased additions of silica. The process did not increase the silica content of the treated water, since all the activated silica was removed by coagulation.

S. R. J. Cotton<sup>5</sup> has provided data to demonstrate that in certain cases sulphuric acid may be a valuable aid in the operation of a coagulation and filtration plant. He reports that its use for adjusting the pH of the Auckland, New Zealand, raw water to 5.8, prior to the addition of aluminium sulphate, permits a reduction of 40—45% in the consumption of the latter chemical. The treatment is for the removal of colour due to a negatively-charged colloid.

### *Sterilising Agents in Water Treatment.*

The use of sterilising agents in water purification, together with other effects of such treatments, such as their effects on taste and colour, continues to attract considerable attention. Chlorination, in various

<sup>4</sup> *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 101; B., 1945, III, 155.

<sup>5</sup> *New Zealand J. Sci. Tech.*, 1945, 26, B, 182; B., 1945, III, 179.



guises, is still the principal subject of investigation in this sphere, but the possibility of achieving the same ends by other methods is not being completely ignored.

G. R. Weber and M. Levine<sup>6</sup> have considered various factors affecting the germicidal efficiency of chlorine and chloroamine. They noted that with chlorine there was a marked lag followed by progressively increasing death rates of bacteria, whereas with chloroamine the rates of death were (except for a short lag) quite consistent throughout the period of disinfection. With concentrations of ammonia of less than one eighth that of available chlorine (hypochlorite), the chlorine residuals were reduced in proportion to the ammonia present, but the nature of the germicide remained essentially that of hypochlorite. On the other hand, with concentrations of ammonia amounting to more than one quarter that of available chlorine, the concentration of available chlorine was only slightly altered, but the nature of the germicide was changed from hypochlorite to chloroamine. The authors also reported that doubling the concentration of available chlorine reduced the killing time by about 50% for chlorine and 40% for chloroamine. A fall of 10° in temperature resulted in a two-fold increase in the necessary period of exposure when employing chlorine and a three- to four-fold increase for chloroamine, to give equivalent germicidal action. Particulars are also given of the effects of excess of ammonia and of changes in pH. It appears that at pH values commonly met with in practice, chlorine as hypochlorite proved a much more efficient germicide than did chloroamine.

Mlle. Dudevant and E. Lasausse<sup>7</sup> consider chloroamine to be preferable to hypochlorite, as having more regular action, more resistance to catalytic destruction, lower cost as smaller concentrations can be used, and less tendency to give rise to a noxious taste or odour. These workers discarded the normal "chlorine equivalent" method of ascertaining the amount of active chlorine required to treat drinking water; in its place they used a bacteriological count of coli, a standard value of 10 coli per litre of treated water being accepted as satisfactory.

A valuable contribution on break-point chlorination has been submitted by A. T. Palin.<sup>8</sup> The paper contains a very able assessment of the present state of knowledge on this subject, and concludes with a useful bibliography. Some interesting points were raised in the discussion of the paper, touching on matters which have as yet received little attention. For example, in his reply to the discussion, Mr. Palin said that little was known about the physiological effect of drinking water containing small amounts of chlorine, chloroamine, and other chloro-compounds. So far there appeared to be no record of any injurious effect having resulted from the continued drinking of chlorinated water, but it was an aspect of chlorination which merited attention. Dealing with questions on

<sup>6</sup> *Amer. J. Publ. Health*, 1944, **34**, 319; B., 1944, III, 267.

<sup>7</sup> *J. Pharm. Chim.*, 1941, [ix], **1**, 397; B., 1945, III, 179.

<sup>8</sup> *J. Inst. San. Eng.*, 1945, **44**, 98.



other aspects of chlorination, the author said that he had no evidence of chlorination affecting water softening, either by the lime-soda process or by zeolites in domestic plants, but he thought the possible effects of chlorine on the more recently developed resins might well be investigated.

An interesting report on the use of chlorine dioxide in water treatment has come from J. F. Synan, J. D. Macmahon, and G. P. Vincent.<sup>9</sup> As chlorine dioxide is a more powerful oxidising agent than chlorine, higher concentrations are required for the disinfection of polluted waters, even though its bactericidal power is greater than that of chlorine. They report that it is more effective than chlorine or chlorine-ammonia treatment for eliminating tastes and odours. The authors also claim that the use of chlorine for disinfection only, followed by chlorine dioxide for odour control, has proved effective and economical.

W. W. Smith and R. E. Bodkin<sup>10</sup> have investigated the influence of pH on the bactericidal action of chlorine and of ozone. It has been found that comparatively low concentrations of ozone will bring about the rapid destruction of the virus poliomyelitis and cysts of *Entamoeba histolytica*, whereas chlorine at higher concentrations was ineffective. Comparing the bactericidal action of ozone with that of chlorine at various pH values, it was found that over a wide range ozone was many times as effective as chlorine. Also, changes in pH value had less effect on the bactericidal power of ozone than on that of chlorine.

The potentialities of ultra-violet energy as a water disinfectant using special lamps has been gone into by M. Luckiesh and L. L. Holladay,<sup>11</sup> who note that this method has particular claims to consideration when automatic disinfection is desired and chemical treatment might prove objectionable. After giving particulars of experimental procedure and mentioning facts which influence the process, the authors give one or two specific illustrations of its performance. At Cleveland six inches of water in a tank one foot square is disinfected by means of an 8-watt lamp in a reflector above the tank; 80 gallons of tap water can be disinfected per hour with a *Bact. coli* survival of only 0.01%. By means of an experimental U-shaped 4-watt lamp immersed in about 2 quarts of water, almost all the *Bact. coli* were destroyed in two minutes. The output of energy is reduced when the lamp is immersed in water, because of the lowering of temperature. The authors also describe a simple method for disinfecting water in a pressure system.

The promising results reported from the use of other methods, some of which have given good (but usually expensive) performances in isolated cases in the past, may foreshadow the breaking of the practical monopoly of chlorine and chlorine-ammonia for water sterilisation. Cheaper power and improved methods of operation could put a very different complexion on this subject.

<sup>9</sup> *J. New England Water Works Assoc.*, 1944, 58, 264; B., 1945, III, 115.

<sup>10</sup> *J. Bact.*, 1944, 47, 445 (abstract).

<sup>11</sup> *Gen. Elect. Rev.*, 1944, 47, No. 4, 45.



### *Filtration of Water.*

An interesting development in the technique of water filtration has been described by N. J. Pugh<sup>12</sup> in a paper dealing with the treatment of doubtful waters for public supplies. At the Ryton waterworks of the Coventry Corporation, a river water of rather poor and variable quality is prepared for public supply. The many problems arising have been scientifically and determinedly tackled, but the operation of break-point chlorination (which has proved effective in other respects) is upset from time to time by the high ammonia content of the raw water. In an attempt to control the ammonia content, experiments have been made with a "nitrifying filter" having filtering medium of much coarser grade than that normally used in water purification practice. In fact, it is designed and operated on similar lines to the "cyclo-nitrifying filter" evolved by J. H. Edmondson and S. R. Goodrich for the improvement of sewage works effluents, and mentioned in last year's Report (p. 491). The experimental filter has a depth of 8 ft., the size of material varying from  $\frac{1}{4}$ — $\frac{3}{8}$  in. in the top layer to 4—6 in. at the bottom. The author reports that the results of the preliminary work have been so encouraging (dosages of the order of 1500 to 2000 gallons per cubic yard per day have already been successfully treated) that a nitrifying filter of 750 cubic yards capacity is being constructed. This application of the principles of sewage purification to water treatment gives point to the comment, already made, on the growing field of interest common to both services.

H. H. Black and C. H. Spaulding<sup>13</sup> have given particulars of portable water filters, employing diatomaceous earth instead of sand, for the use of field troops. These filters are much lighter in weight than the ordinary sand-filled type, and are reported to be more efficient in their removal of the chlorine-resisting cysts of *Entamoeba histolytica*. To ensure water of good bacterial purity, coagulation with alum prior to filtration is necessary. The construction and working of filters specially designed to use diatomite are described in the paper.

### *Lime-Soda Process of Water Softening.*

One of the disadvantages of the lime-soda process of water softening is the disposal of the considerable quantities of "lime sludge" produced. Accumulations of this waste product have often proved a serious embarrassment. The utilisation of the sludge has been the subject of some research and much speculation. From America, where the dewatering and calcining of the sludge is receiving attention, there have come reports of work which may interest those concerned with this problem.

H. V. Pederson<sup>14</sup> has described a calcination process which is claimed to be successful. After separation in a continuous centrifuge the lime

<sup>12</sup> *Trans. Inst. Water Eng.*, 1945, 50.

<sup>13</sup> *J. Amer. Water Works Assoc.*, 1944, 36, 1208; B., 1945, III, 30.

<sup>14</sup> *Ibid.*, 1170; B., 1945, III, 31.



sludge is flash-dried. Its fineness is then such that 99.8% passes a 325-mesh and 20% a 3000-mesh sieve. This material is next calcined in a stationary kiln, by allowing it to fall 7 or 8 ft. on to a plate inclined at 60° to the horizontal, whence it splashes into the hottest part of a flame in a parallel chamber. Separation of iron and magnesium compounds is effected, as they adhere to the walls of the kiln and can be removed each day. The recovered lime sludge is reported to have proved satisfactory for water softening. The author regards this process of flash-calcination as being well suited for small water-treatment plants because it can be worked intermittently. Indeed, it appears doubtful whether it could be worked any other way.

Bearing on the same subject, F. G. Nelson<sup>15</sup> has contributed information on the continuous centrifuging of lime sludge. He reports that by this method the sludge can be concentrated to about 61% of solids, and magnesium allowed to pass to waste. He also states that carbonation of the sludge before thickening aids the removal of magnesium and improves settlement and centrifuge operation.

#### *Ion Exchangers in Water Treatment.*

Probably the most interesting development in this field during the year has been the publication of methods worked out during the war for the preparation of drinking water from sea water. The problem itself is, of course, a very old one, for next to the sea itself, thirst has always been the biggest enemy of those who have suffered shipwreck. The matter assumed much larger proportions during the war, when both seafarers and airmen were being forced to take to the sea in small boats and rubber dinghies. The problem of supplying these unfortunates with drinking water was energetically tackled, and satisfactorily solved.

Some good work was done in the improvement of sea-water stills, resulting in the production of satisfactory equipment for ships' life-boats, but distillation is not a suitable process for operation in rubber dinghies. Accordingly, after consultations between various Government departments and other bodies, work was put in hand to provide an alternative method for this purpose. It appears that the chief credit for evolving a satisfactory process must be given to the staffs of the Water Pollution Research Board and of the Permutit Company, working in close collaboration. H. Ingleson<sup>16</sup> has given a most interesting account of the many problems which arose in the investigations, and of the ways in which the difficulties were overcome. Many requirements had to be met, besides that of efficient purification capacity; for example, compactness, stability, and ease of operation. The reagent ultimately supplied, in briquette form, had the following composition by weight: silver zeolite 79.1%, barium hydroxide octahydrate 9.5%, silver oxide 0.5%, fuller's earth 9.0%, graphite 1.9%.

<sup>15</sup> *J. Amer. Water Works Assoc.*, 1944, 36, 1178; B., 1945, III, 31.

<sup>16</sup> *J.S.C.I.*, 1945, 64, 306; B., 1946, III, 35.



The same subject has also been dealt with by E. I. Akeroyd, E. L. Holmes, and A. Klein.<sup>17</sup> Their contribution includes a detailed description of the apparatus used in practice. The sea water and the reagent are shaken in a flexible bag of rubberised fabric, which is fitted with a permanent filter cloth. The drinking water is strained off by squeezing the flexible bag, thus forcing the water through the filter cloth. A feature of the apparatus is the ingenious way in which all the necessary items have been arranged into a compact and convenient pack. The authors state that the resulting apparatus can provide six times as much water as could be carried in a container of the same size.

Other methods for obtaining drinking water from sea water have been described, but they have hardly the same interest as that used in practice. One or two of the processes do not appear very suitable for use by inexperienced operators, working under trying conditions. In untutored hands, they might conceivably solve the thirst problem by poisoning the drinker.

Experiments on the purification of water by the use of synthetic ion exchangers, using pH for control purposes, have been described by A. L. Kenworthy and J. N. Howard.<sup>18</sup> In the experiments two sets of towers packed with Amberlite resins were used. One contained the cation-exchange material IR<sub>1</sub>, the other IR<sub>100</sub>; IR<sub>4</sub> was used as anion-exchange material in both sets. Tap water was passed through the towers at various rates. Quantitative spectrographic analyses were made for copper, lead, and zinc, and comparative spectrographic analyses were made for iron, manganese, magnesium, sodium, and calcium. Total solids were determined conductometrically. It was found that the pH value of the water remained constant until the cation-exchange material was saturated; it then rose rapidly. This break-through point was sharply defined, particularly at the lower rates of flow. Hydrochloric acid and sodium carbonate were used for regenerating the resins. Water which had passed through the Amberlite resins was found to be comparable with distilled water as to its content of cations, and in several respects it was equal to water redistilled from a glass still.

#### *Fluorine in Water Supplies.*

The influence of the fluorine content of water supplies on the dental health of the consumer is still receiving active attention. Present opinion seems to favour about 1 p.p.m. of fluorine as the ideal concentration. Some towns having waters markedly deficient in fluorine, as judged by this standard, are considering increasing the fluorine concentration; others, with supplies containing excessive amounts of this element, are interested in methods for its diminution. Much information on this subject has been collected in a report of the Board of Health, Brantford, Ont.,<sup>19</sup> in which it is noted that recent research has indicated

<sup>17</sup> *Water & Water Engr.*, 1945, 48, No. 594, 556.

<sup>18</sup> *Soil Sci.*, 1944, 57, 293; C., 1944, 189.

<sup>19</sup> *Eng. Contr. Rec.*, 1944, 57, No. 16, 58.



a relation between dental health and the amount of fluorine ingested. The water supply of Brantford contains no fluorine. The case of Oakley, Idaho, is instanced as evidence of the influence of fluoride on dental health. Until twenty years ago, the inhabitants of this town received water containing 6 p.p.m. of fluorine, and dental fluorosis was prevalent. In 1925 the water supply was changed and a supply free from fluorine was provided; young children examined in 1933 showed complete absence of dental fluorosis. On the other hand, the report mentions that in several countries it has been noticed that the incidence of dental caries is less in regions where dental fluorosis occurs. Seeking the happy mean, the report quotes evidence to show that in communities receiving water with a fluorine content of about 1 p.p.m. the incidence of dental caries and the prevalence of fluorosis are both very slight. Accordingly it recommends that this amount of fluorine should be added to the water supply of Brantwood. Nevertheless, the Board are awake to the fact that many factors—physiological and otherwise—connected with the administration of fluorine are still in need of exploration.

R. Weaver<sup>20</sup> has recounted his observations on Tyneside. The water supply of North Shields contains less than 0.25 p.p.m. of fluorine, whereas South Shields water (derived mainly from deep wells in magnesian limestone) carries about 1.4 p.p.m. General conditions in the two towns are so similar that it is unlikely that their dietetic habits differ greatly. Nevertheless, there is evidence of a striking difference in dental well-being, for when examinations were made of 1000 school children from each town, it was found that the incidence of dental caries in 12-year-old school children from South Shields was only 56% of that in children of the same age from North Shields. The author has some justification for his opinion that intake of fluorine is probably the decisive factor.

A patent of the Resinous Products & Chemical Company<sup>21</sup> is designed to aid those who suffer from the opposite trouble—a superfluity of fluorine. This claims efficient removal of fluorine by passing the water upwards through an anion-exchange granular resin, impregnated with an aqueous solution of an aluminium salt. The resin employed is of the phenol-formaldehyde type, having nuclear substituents, such as a polyalkylenepolyamine resin chiefly in its basic form.

#### *Water Analysis.*

A photometric method for the determination of lead has been described by A. V. A. Munton, H. H. Wittenberg, and G. K. Crowell.<sup>22</sup> The method is based on the extraction of the lead with dithizone in chloroform, in the presence of aqueous ammonia, potassium cyanide, and citric acid; it is subject to interference by only bismuth, thallium, and stannous tin. The authors report that standardisation of the volumes used makes only one extraction necessary.

<sup>20</sup> *Brit. Dent. J.*, 1944, 76, 29; A., 1944, III, 198.

<sup>21</sup> B.P. 569,307; B., 1945, III, 200.

<sup>22</sup> *J. Amer. Water Works Assoc.*, 1945, 37, 207; C., 1945, 192.



Another method for the determination of lead in water or fine chemicals, this time by means of a spot reaction, has come from F. Feigl and N. Braile.<sup>23</sup> On the addition of sodium mercuric sulphide and ammonium chloride, the precipitated mercuric sulphide carries down the relatively small amount of lead sulphide; the mixture is filtered, and the precipitate moistened with hydrogen peroxide, dried, gently ignited, and cooled. Lead sulphate can be detected by the formation of red rhodizonate of lead when a solution of sodium rhodizonate and a buffer solution are added to the residue. The method will detect lead in a dilution of 1 in 100 millions. By comparison of the colour with those obtained from standard lead solutions, moderately accurate quantitative estimations are possible.

G. N. Bond<sup>24</sup> has drawn attention to the necessity of carrying out titrations for dissolved oxygen in water, by Winkler's method, at temperatures below 70° F.; above that temperature the sensitivity of the starch solution is affected, giving low values for dissolved oxygen.

Noting that the detection of ammonia by direct nesslerisation suffers from interference by alkaline-earth metals, A. Nau<sup>25</sup> has suggested a simple method for their removal; he recommends the addition of about 12 drops of a 10% solution of disodium phosphate to 10 ml. of the sample, and centrifuging.

#### *Bacteriology and Biology of Water.*

Some work by W. M. Wallace<sup>26</sup> has emphasised the undesirability of dead ends in water distribution systems; in this case the bacteriological aspect was investigated. He found that both the number of organisms and the number of types in the dead ends of the mains carrying a chlorinated water were greater than in the water fed to the mains. No significant change resulted from the substitution of chlorine-ammonia treatment in place of chlorination. The number of organisms found increased with the temperature of the water. Of 448 Gram-negative rods isolated, 146 were coliforms, 92 *Alcaligenes*, 57 *Pseudomonas*, 59 *Proteus*, 43 *Eberthella*, and 20 *Salmonella*. The only organisms found which were actually associated with an instance of illness resembled *Proteus morganii*. The author considers it probable that the organisms gain entry to the system through cross connexions, leaks, repairs, etc.

A. T. Palin<sup>27</sup> has described the methods which were tested to counter an outbreak of *Euglena* at Coventry's Ryton waterworks. At this plant, water taken from the river is treated with aluminoferric and pumped to upward-flow sedimentation tanks having a retention period of 2½ hours; the water is then passed through rapid sand filters and treated with chlorine and ammonia. The normal period of contact of the chlorine and ammonia

<sup>23</sup> *Analyst*, 1944, 69, 147; C., 1944, 109.

<sup>24</sup> *J. S. African Chem. Inst.*, 1944, 27, 25; C., 1945, 128.

<sup>25</sup> *Chem. Zentr.*, 1943, I, 1705.

<sup>26</sup> *J. Amer. Water Works Assoc.*, 1944, 36, 1356; B., 1945, III, 84.

<sup>27</sup> *Water & Water Eng.*, 1944, 47, 263.



with the water is 4 hours. In October, 1943, there was a sudden outbreak of *Euglena* in the raw, settled, and filtered waters. After laboratory experiments with various methods of treatment, the process selected for use on the works was treatment with 3 grains of aluminoferric per gallon and 5 p.p.m. of chlorine, the reagents being added together (simultaneous dosing with the two chemicals was found to be important). The paper also describes several supplementary investigations bearing on the treatment of the infected waters.

#### ATMOSPHERIC POLLUTION.

The Atmospheric Pollution Research Committee of the Department of Scientific and Industrial Research<sup>28</sup> have given details of a method of making rapid surveys of atmospheric pollution. These rapid surveys are of value for indicating the distribution of pollution in an area, but not for determining changes in the degree of pollution. For convenience the polluting matter can be divided into three categories—coarse matter, smoke, and gases. The coarse matter is determined by weighing the deposits collected in Petri dishes in 48 hours. Smoke is determined by drawing a measured volume of air through a filter-paper; the area of the stain and its blackness are compared with standards. Gases, amongst which sulphur dioxide is of major interest, cannot be determined as quickly as the other polluting bodies.

#### AIR PURIFICATION.

The use of germicidal mists and vapours in air disinfection has been studied by A. H. Baker and C. C. Twort.<sup>29</sup> The authors define the terms durability, persistence, and stability, as applied to mists. A comparison of the durability of nine heat-volatilised phenols confirmed the superiority of hexylresorcinol. They find that both vapour and mist are necessary for bactericidal efficiency. Vapour pressure is the most important property of a phenolic germicide; there is little correlation between phenol coefficient and activity as mist or vapour. Rapidity of action and durability are incompatible. There was no evidence of specificity of inorganic compounds; mercuric chloride proved bactericidal when dispersed either mechanically or by heat. The bactericidal efficiency of a mist or vapour is measured by the concentration of material required to kill the test organism in ten minutes.

The use of ultra-violet irradiation of the floors and upper air of barracks, as a means of controlling airborne infections in a naval training centre, has been investigated by S. M. Wheeler<sup>30</sup> and his co-workers. The irradiated premises showed a reduction of about 30% in respiratory illness, as compared with adjacent barracks used as a control. Also, bacterial counts from air samples in irradiated barracks showed a reduction

<sup>28</sup> *Analyst*, 1944, **69**, 347; B., 1945, III, 51.

<sup>29</sup> *J. Hygiene*, 1944, **43**, 382; B., 1945, III, 154.

<sup>30</sup> *Amer. J. Publ. Health*, 1945, **35**, 457; B., 1945, III, 215.



of about 50% in total saprophyte colony counts as compared with non-irradiated barracks.

### INSECTICIDES.

It can safely be said that developments in the use of D.D.T. for insecticidal purposes have overshadowed all other recent work in this sphere. Although over-boasted by the lay press—which hailed D.D.T. as the final answer to a host of problems—there is no doubt that the discovery of the insecticidal properties of this compound is an event of outstanding importance—(the compound itself— $\alpha\alpha\alpha$ -trichloro- $\beta\beta$ -di-*p*-chlorophenylethane—was synthesised by Zeidler over seventy years ago).

G. A. Campbell and T. F. West<sup>31</sup> have reviewed the work leading to the development of D.D.T. and given an account of its general properties; they have also considered the practicability of incorporating it in paint products. It has been found that dried films of water paint, whether of the dry distemper or oil-emulsion type, have a marked toxic action on flies even when only 0.5% of D.D.T. is present; with 5% of D.D.T., toxicity is retained almost unimpaired for at least six months. Preliminary trials with oil and varnish paints were not encouraging, but a varnish made by dissolving coumarone resin and D.D.T. in white spirit developed strong toxicity to flies on exposure. In another publication, the same authors<sup>32</sup> commented on the use of D.D.T. for mosquito control. An excellent account of the evolution of D.D.T. has been given by I. M. Heilbron.<sup>33</sup>

Various aspects of the insecticidal uses of pyrethrums continue to receive attention. For instance, R. C. Bushland, G. W. Eddy, and E. F. Knipling<sup>34</sup> have studied synergists for pyrethrum when used against the body louse. The use of "IN-930" (undecenoisobutylamide) in 2% concentration increased the initial toxicity of the pyrethrums about 100 times when used in a pyrethrum-pyrophyllite louse powder. Sesame oil and "D.H.S. Activator" also increased the effectiveness of pyrethrums, but they were not so good as "IN-930" in this respect. All the synergists were by themselves non-toxic to lice at 2% concentration.

M. E. Synerholm, A. Hartzell, and J. M. Arthur<sup>35</sup> have investigated derivatives of piperic acid, in relation to their toxicity to houseflies. They report that esters and substituted amides of piperic acid are useful in this connexion. The most toxic amides are derived from primary or secondary alkylamines containing 3—7 carbon atoms, and the most effective esters from alcohols having 4—6 carbon atoms. The amides and esters have a synergistic action when used with pyrethrins. Esters prepared from phenol and amides from arylamines have relatively small toxicities.

<sup>31</sup> *J. Oil Col. Chem. Assoc.*, 1944, 27, 241; B., 1945, III, 68.

<sup>32</sup> *Chem. and Ind.*, 1945, 154; B., 1945, III, 198.

<sup>33</sup> *J. Soc. Arts*, 1945, 93, 65; B., 1945, III, 68.

<sup>34</sup> *J. Econ. Entom.*, 1944, 37, 485; B., 1945, III, 113.

<sup>35</sup> *Contr. Boyce Thompson Inst.*, 1945, 13, 433; B., 1945, III, 154.



J. R. Holden and G. M. Findlay<sup>36</sup> have stated that anti-mosquito cream Mark II, containing pyrethrum in a vanishing cream base, proved of value as a tsetse fly repellent for at least six hours after application. The repellent action was destroyed by heavy sweating associated with exposure to a strong sun.

#### SEWAGE DISPOSAL.

Sewage undertakings had their full share of war-time worries, some of which are persisting even after the conclusion of hostilities. During the war years, as would be expected, technical staff, manual labour, and materials have all been in short supply. In consequence, research, supervision, and maintenance have suffered, while works reconstruction and extension has been practically at a standstill. Some of the effects of war-time conditions have been exceptionally severe on sewage treatment works. For example, owing to the fact that much of the plant is situated out in the open, deterioration and corrosion are rapid if proper attention is impossible. Also, plant manipulation under black-out conditions was very difficult, a fact which reacted to the disadvantage of many installations.

However, in spite of many difficulties, a reasonably good standard of purification has been maintained at most sewage works. Nevertheless, several writers during the year have drawn attention to the fact that the position is not a happy one, for on many undertakings it is going to be a race against time to carry out necessary maintenance work, or to make extensions to the plant, to avert serious trouble.

In one respect sewage treatment works have been lucky—on the whole they have suffered little damage from enemy action. Spread over a large area and constructed mainly of non-inflammable material, they were a "good risk" from this point of view.

Biological filtration is still attracting close investigation, and very encouraging results have been reported from some of the new variants of this old process. With the development of these processes, and also the possibility of using some of them in conjunction with each other, it is now very difficult to select the best type of plant for each individual scheme. Local conditions, such as strength of sewage, nature of existing plant, levels, and available site area, will probably be the decisive factor in many instances.

Investigations are also in hand on several other subjects, for instance, sedimentation, sludge treatment, and analytical standards for sewage effluents, but all-round progress cannot be rapid until more scientists are available.

The present position in sewage disposal was ably surveyed by J. H. Edmondson<sup>37</sup> in his Presidential Address to the Institute of Sewage Purification. He placed special emphasis on the fact that, if proper use

<sup>36</sup> *Trans. R. Soc. trop. Med. Hyg.*, 1944, 38, 199; B., 1945, III, 215.

<sup>37</sup> *J. Inst. Sewage Purif.*, 1944, 7.



is made of modern developments, a sewage treatment plant can be efficient, compact, and of pleasant appearance, doing no damage to the amenities of the district in which it is situated. As far as American publications are concerned, H. Heukelekian<sup>38</sup> and his collaborators have provided a useful review of the literature of 1944 on sewage and trade waste treatment and stream pollution.

### *Sewerage.*

With the projected establishment of new towns, and in view of the housing developments which are imminent in most areas, policy on the design of sewerage systems assumes added importance. On some points there can be no dispute; for example, provision must be made for accepting all domestic sewage and trade wastes into the sewers. In many cases the most troublesome problem is that of deciding on the best method of dealing with surface water.

The combined system of sewerage has come in for much criticism. Under this system, sewage, trade effluents, and rain water are all connected to the same sewer. Then, to relieve the sewer during times of heavy rain, overflows are placed at strategic points on its course. These overflows, which are usually intended to come into operation at six times the dry weather flow, discharge a mixture of sewage and rain water to the nearest water course, often with disastrous consequences.

As an alternative, separate and partly separate systems of sewerage can be employed. The aim of these systems is to collect the rain water in a separate sewer and convey it direct to the water course. Thus, in theory, with a separate system of sewerage, storms do not cause any pollution of the water course or have any effect on the sewage passing to the sewage works. This ideal solution would often be difficult and expensive to attain in practice. A common compromise is to pass the water from the street and the front of houses into a surface water sewer, while allowing the drainage from back yards to enter the foul sewer.

There have been many arguments as to the merits and demerits of the different systems of sewerage. The present trend seems to be strongly towards separate or partly separate systems; one of the main reasons for this is the gross pollution of streams which frequently takes place from the storm overflows of combined sewers. These overflows are often badly designed, wrongly set, and inadequately maintained, with the result that filthy liquors are discharged to the streams; it is by no means uncommon to find these overflows functioning at peak flows even in dry weather. The modern opinion is that once a liquid has been put into the foul sewer, it should not be discharged to a stream without treatment.

A word of warning may not be out of place here. The mere adoption of a policy of separate or partly separate sewerage is not in itself a sufficient safeguard. Continual vigilance is needed to ensure that no

<sup>38</sup> *Sewage Works J.*, 1945, 17, 223; B., 1945, III, 179.



improper connexions are made to the surface water sewer, for it is obvious that if, through wrong connexions, crude sewage or trade wastes were conveyed direct to the water course, the consequences might well be serious.

A thoughtful contribution to this thorny topic of storm water disposal was made by M. Lovett<sup>39</sup> when discussing the past, present, and future of sewerage and sewage disposal.

The disintegration of concrete and cement in sewerage systems has caused concern at many places both at home and abroad, particularly where high temperatures or the presence of certain trade wastes have encouraged the decomposition of sulphur compounds. A mass of most useful information on this subject has been collected and co-ordinated by C. Hammerton.<sup>40</sup>

#### *Oil and Grease in Sewage.*

There have been numerous reports, both here and in America, of troubles caused through the discharge of oil and grease to sewers. The difficulties attributable to oils and greases cover practically the whole field of sewerage and sewage treatment, varying from sewer troubles to the overloading of skimming devices on sedimentation tanks, the upsetting of sludge digestion plants, and the deterioration in the quality of the final effluent due to deleterious effects on the biological purification plants. In a mass of literature bemoaning the troubles caused by oil and grease wastes—and this type of trouble is undoubtedly serious and increasing—just one or two small compliments are found. For instance, R. M. Bolonius<sup>41</sup> reports that small amounts of casein paints assist the activated-sludge plant at Lancaster, Pa., the "slate flour" filling considerably increasing the density of the sludge; in the same contribution, however, the author notes that the discharge of frequent large quantities of oxidising or drying and mineral oils has an adverse effect on the activated-sludge and sludge-digestion processes at that town.

The effects of oils and greases on sewage treatment plants have also been considered by F. G. Nelson and W. N. Lauer.<sup>42</sup> After discussing the ill effects of grease (often best removed at the source) they give a brief description of an apparatus for removing grease from sewage by the vacuum flotation process. They report that, so long as excessive quantities of mineral oil are not present, grease can be disposed of by digestion. Following thorough experimentation on the latter point, W. Rudolfs<sup>43</sup> found that in some ways moderate amounts of grease were beneficial to the sludge-digestion process; for instance, he confirmed that grease decomposed more rapidly than other organic matter and assisted gas production.

<sup>39</sup> *Surveyor*, 1945, **104**, 587.

<sup>40</sup> *J. Inst. Sewage Purif.*, 1944, 150; B., 1946, I, 295.

<sup>41</sup> *Sewage Works J.*, 1945, **17**, 506; B., 1945, III, 199.

<sup>42</sup> *Ibid.*, 1944, **16**, 1105; B., 1945, III, 114.

<sup>43</sup> *Ibid.*, 1125; B., 1945, III, 114.



From time to time various methods have been suggested for the separation of oil and grease from sewage. Flotation by diffused air (or air and chlorine) has received encouraging reports, but there have been differences between the opinions of various observers. Flocculation and chemical treatment (particularly with iron salts) have also received some attention in America. In this country certain towns in the textile districts of the West Riding of Yorkshire, where the sewage contains much grease derived from wool washing and piece scouring, have for many years successfully employed acid cracking followed by sedimentation. The grease can then be recovered from the sludge, for purification and re-sale.

#### *Sedimentation in Sewage Treatment.*

The removal of settleable solids is a very important process in sewage purification, both in preparing the sewage for treatment by biological processes and in fitting the biological effluents for final discharge to the stream. In the main the difficulties inherent in the sedimentation of sewage and sewage effluents arise—like many others in sewage treatment—from the unstable and variable nature of the sewage, and from changes in the rate of flow. At many sewage plants, these variables fluctuate violently and often unpredictably, a fact which makes the design of sedimentation tanks a matter of great complexity. In this connexion it is worth emphasising that the sewage works operator has little control over his raw material. Whatever the nature and volume of sewage reaching the works, it must be processed at once. It cannot be warehoused or put into storage until required, for its huge volume and its proneness to objectionable decomposition put a narrow limit on this procedure. A little can be done in the way of levelling out variations in the strength and rate of flow, mainly by means of providing storage capacity and utilising various “balancing” devices, but at most works it is impossible to work the plant at anything approaching a steady load. The production of sewage varies from hour to hour, while the vagaries of the weather are beyond control. Furthermore, in industrial areas, the discharge of process waters is often a most potent and variable factor.

The nature of the sewage solids is also worth a word of comment. They vary from mineral grit to finely divided matter such as suspensions of clay, while the organic matter ranges from coarse particulate matter down to minute specks and colloidal suspensions.

In view of these and other complications, it is small wonder that attempts to apply the theories of sedimentation, particularly in continuous flow tanks, have to be tempered with compromises and modified to suit the conditions arising in works practice. Nevertheless, in spite of all the difficulties, the applicability of theory is being increasingly considered, and settling tank design is being steadily improved. The increased use of mechanical devices for flocculation and for the removal of scum and settled sludge is proving a great aid in this connexion.



T. R. Camp<sup>44</sup> has made a noteworthy contribution on the application of theory to sedimentation practice. After carefully reviewing the principles and theory of the subject, mainly from the mathematical angle, he put forward tentative proposals for the design of primary sedimentation tanks on that basis.

Flocculation by both chemical and mechanical devices is again coming to the fore as a topic for investigation. The use of chemicals to assist sedimentation has serious drawbacks, such as expense and the production of large amounts of sludge, and is usually employed only with abnormal industrial sewages or to meet special emergencies, but mechanical flocculation, possibly in conjunction with a small dose of chemicals, may ultimately prove to justify wider application.

The problems of sedimentation on sewage works are not confined to persuading the solids to settle; there is the further task of ensuring that they do not rise again, for these light, largely organic solids are easily floated by such agencies as entrained gas bubbles or by changes in the specific gravity of the liquid. Lifting by gas bubbles is a common cause of trouble, particularly when (as in summer) the liquid is warmer, and bacterial action therefore more intense. It has long been known that anaërobic decomposition of organic matter, resulting in the evolution of methane and other gases, was the cause of many sludge-rising troubles in primary sedimentation tanks. Another type of reaction which has received attention in more recent years is the flotation of sludge by gaseous nitrogen liberated by the bacterial reduction of nitrates and nitrites. Three very interesting papers on this subject were presented at a meeting of the Institute of Sewage Purification. The first, by T. W. Brandon and J. Grindley,<sup>45</sup> dealt with the influence of nitrate (in the form of ammonium nitrate, discharged to the sewers from a munition factory) on primary sedimentation. In the second paper, L. F. Mountfort<sup>46</sup> recounted his experiences in the rising of sludge in the humus tanks following percolating filter treatment, while in the third contribution W. T. Lockett<sup>47</sup> gave some interesting information on the behaviour of sludge in the final settlement tanks of activated-sludge plants. It may be profitable to compare the findings of the three papers. In the work of Brandon and Grindley, concentrations of nitric nitrogen up to about 1 part per 100,000 did not cause trouble in the crude sewage settling tanks, but above that figure complications arose. Mountfort's observations at the East Middlesex sewage works indicated that no serious sludge-rising troubles occurred in the humus tanks when the amount of nitric nitrogen did not exceed 3 or 4 parts per 100,000, but when, owing to changes in the nature of the sewage, the figure increased to 5 or 6 parts per 100,000, sludge flotation assumed serious proportions. Lockett

<sup>44</sup> *Proc. Amer. Soc. Civil Eng.*, 1945, 71, 445; B., 1945, III, 155.

<sup>45</sup> *J. Inst. Sewage Purif.*, 1944, 175; B., 1946, III, 186.

<sup>46</sup> *Ibid.*, 170; B., 1946, III, 186.

<sup>47</sup> *Ibid.*, 180; B., 1946, III, 186.



considers that sludge-rising troubles in the final settling tanks of the activated-sludge system process are mainly prevalent in a fairly well defined range of nitric nitrogen concentration. If no nitrate is present, or if the amount exceeds about 0.8 part per 100,000, nitrogen flotation of the sludge does not usually occur; the danger is greatest when the nitric nitrogen is present in small quantities—less than 0.8 part per 100,000. It therefore appears that this phenomenon varies with sewage at different stages of purification, and with effluents from different types of purification plant. Coupled with the fact that sewages of various types probably also have their individual peculiarities in this connexion, the designers and operators of settling tanks are faced with a pretty problem.

### *Biological Filtration of Sewage.*

Research on biological filtration, which has shown such marked increase in the last few years, is still very active. Much important information has come to light, and will no doubt be increasingly applied to works practice.

H. Heukelekian has carried out some interesting work on the composition and properties of filter film, making comparisons between a conventional filter and a high-rate plant employing recirculation of effluent. Considering first the accumulation of film,<sup>48</sup> he found that in both filters the quantity of film was greater in winter than in summer. In winter the maximum quantity of film in the standard filter was at the top, whereas in the high-rate filter it was below the surface. From other observations he concluded that insect larvæ played a less important part in the high-rate filter than they did in the conventional filter. The second portion of the study<sup>49</sup> dealt with the biochemical characteristics of filter film. Amongst other interesting data there is the observation that the chemical characteristics of the conventional filter film and activated sludge are more nearly alike than those of the high-rate filter film and activated sludge. Temperature also played an important part in determining the characteristics of the film. The author's third contribution<sup>50</sup> dealt mainly with the nitrifying capacity of the film. He found that nitrifying organisms were well established in both filters, and that the highest nitrifying capacity occurred in the top 2 ft. of each bed. The latter opinion is interesting, for in this country it is usually assumed (and observations from several plants support the view) that most nitrification takes place in the lower layers of the filter beds. The weaker nature of American sewages may have a bearing on this point.

Methods of intensifying the activity of filters—in other words, getting more work from each cubic yard of filter medium—continue to attract investigation. J. T. Thompson and H. Watson<sup>51</sup> have drawn attention

<sup>48</sup> *Sewage Works J.*, 1945, 17, 23; B., 1945, III, 134.

<sup>49</sup> *Ibid.*, 269; B., 1945, III, 179.

<sup>50</sup> *Ibid.*, 516; B., 1945, III, 199.

<sup>51</sup> *J. Inst. Sewage Purif.*, 1944, 65; B., 1946, III, 187.



to the improved performance which results from steady distribution of the sewage to the filters. They found that larger volumes of sewage could be purified if the dosage was spread over the 24 hours of each day; also efficiency was increased by using a system of distribution which applied frequent small doses to each portion of the bed, as compared with a system which applied heavy doses at long intervals.

A. Hunter and T. Cockburn<sup>52</sup> have reported on the operation of a works-scale enclosed aërated filter at Glasgow. This filter treated sewage at slightly more than double the rate of the conventional filters on the same works, and produced an effluent of rather better quality. These results were hardly as good as those reported from other enclosed aërated filters. Possibly this was due to the copious surface growth which occurred on the Glasgow filter, a phenomenon not observed to anything like the same extent on other plants of this type. It was suggested in discussion that the Glasgow filter possibly suffered because of its greater depth—18 ft. as compared with about 12 or 13 ft. in other enclosed aërated filters. There was some evidence that in the case of very deep filters little work might be obtained from the lower layers, thus depressing the overall performance.

The Water Pollution Research Board are continuing their works-scale investigations on alternating double filtration and on recirculatory filtration. As several points on applicability to actual works conditions remain to be cleared up, it is yet too soon to give an accurate assessment of the practical capabilities of all the modern modifications of filter technique. It would appear, however, that granted reasonably favourable conditions, alternating double filtration, recirculatory filtration, and enclosed aërated filters are all able to treat sewage at about three times the rate of an ordinary filter, with the production of effluents of the same quality in most respects. The point on which most high-rate filtration processes differ from the conventional filter is that they produce a much lower degree of nitrification. This has led to some controversy as to the importance, or otherwise, of nitrate in sewage effluents. Remembering that nitrates do not yield their oxygen to biological reactions until practically the whole of the dissolved oxygen is exhausted, it would seem that nitrate is of little or no value in keeping a stream in really good condition, for instance, capable of supporting fish life. On the other hand, a reserve of nitrate is probably valuable in streams of poor quality, in preventing the development of objectionable anaërobic decomposition. This view is taken by R. Eliassen<sup>53</sup> in an article in which he probes the significance of certain tests commonly employed for assessing the quality of sewage works effluents.

#### *The Activated-Sludge Process.*

The activated-sludge process has continued to figure prominently in

<sup>52</sup> *J. Inst. Sewage Purif.*, 1944, 12; B., 1946, III, 186.

<sup>53</sup> *Water Works and Sewerage*, 1944, 91, 219; B., 1945, III, 67.



American technical literature, but publications on this subject have not recently been numerous in this country.

G. A. Rohlich<sup>54</sup> has given some interesting information on the determination and significance of oxidation-reduction potential measurements in activated sludge and activated sludge-sewage mixtures. He finds that the oxidising intensity of activated sludge is unaffected within the range of dissolved oxygen usually encountered; the  $E_h$  value remains at a highly oxidising level until the dissolved oxygen falls below 1.0 p.p.m., when  $E_h$  decreases gradually. The  $E_h$  value of activated sludge-sewage mixtures undergoing aëration increases as the sewage undergoes oxidation, and the rapidity of this increase depends on the concentration of oxidisable matter present. The mixture having the higher concentration of impurity has the lower  $E_h$  value, and the subsequent rise in  $E_h$  is slower. Correlation exists between the state of oxidation, as measured by the rate of oxygen utilisation, and the  $E_h$  value, in laboratory and plant experiments. The author's results may have important repercussions in practice, particularly as they are supported by certain well known characteristics of activated-sludge plants, such as the beneficial effects of sewages diluted by rain. They may be taken as supporting the advisability of adequate pretreatment in advance of the aëration plant. They also throw doubt on the contention that when activated-sludge treatment and percolating filters are used in series, the activated-sludge plant should constitute the primary stage. The results draw attention to the possibilities of activated-sludge treatment as a secondary stage, or for such purposes as giving a "quick polish" to percolating filter effluents which are of sub-standard quality.

G. M. Ridenour and J. Greenbank<sup>55</sup> have investigated the effects of cyanide and case-hardening and of copper and zinc plating wastes on the activated-sludge process. Their report includes details of the influence of various concentrations of the wastes on the properties of the activated sludge. It is interesting, and perhaps somewhat unexpected, to learn that the activated-sludge processes quickly recovered even after receiving excessive amounts of certain of these wastes.

High-rate activated-sludge treatment of sewage has been discussed by E. S. Chase.<sup>56</sup> He dealt with the theory and operation of plants using a short aëration period and a relatively low sludge concentration, and producing effluents intermediate in quality between plain sedimentation and normal activated-sludge treatment.

On the operational side, W. H. Wisely<sup>57</sup> has given a comprehensive review of the methods and observations employed in controlling twenty-five American activated-sludge plants. The notes cover a wide field of

<sup>54</sup> *Sewage Works J.*, 1944, 16, 540; B., 1945, III, 30.

<sup>55</sup> *Ibid.*, 774; B., 1944, III, 268.

<sup>56</sup> *Ibid.*, 878; B., 1945, III, 52.

<sup>57</sup> *Water Works and Sewerage, Ref. and Data Sect.*, 1944, 91, R-211; B., 1945, III, 115.



subjects, varying from sludge index to diffuser maintenance, and from bloodworms to rising sludge.

### *Treatment and Disposal of Sewage Sludge.*

The dewatering and ultimate disposal of sewage sludge continues to attract the close attention which its importance justifies.

A. L. Genter<sup>58</sup> has described an interesting method for computing the amount of coagulant required to condition sewage sludge. He paid particular attention to the use of ferric chloride for this purpose. Noting that the ferric chloride demand varies greatly with different types of sludge, and also at different plants, he said that the total requirement of ferric chloride is made up of the demand for the liquid portion (chiefly due to bicarbonate alkalinity) and a demand for the solid portion of the sludge (depending on the ratio of volatile matter to ash). On this basis, he evolved a method for calculating the dosage of ferric chloride required. The formula contains an empirical constant, which is said to usually have a value of about 1.6, but may vary between one and three times this value, according to circumstances. Incorporating such a variable constant, the formula can hardly be claimed to eliminate trial and error methods.

A symposium held by the American Society of Civil Engineers<sup>59</sup> brought out information on a wide range of methods for concentrating sewage sludges. Representatives from several cities gave their experiences in the use of such methods as chlorination, the addition of inert materials, flotation, chemical treatment, and centrifuging.

The investigation of sludge dewatering methods, more rapid and compact than drying on beds, is still active in this country, although publications on the subject are not very numerous. J. M. Wishart, C. Jepson, and L. Klein<sup>60</sup> have given some particulars concerning vacuum filtration of sludge, and their work on this subject at Manchester is continuing.

The manurial value of sewage sludge is now receiving more systematic study. This is well, for increasing knowledge of both the value and the limitations of this product will undoubtedly lead to its more effective utilisation in agriculture. E. M. Crowther and A. H. Bunting<sup>61</sup> have issued a further report of work carried out under the Agricultural Research Council. One of the many interesting points in their paper was the demonstration that digested sludge is a more useful manure than the undigested product. Although some nitrogen is lost during digestion, the loss of carbon is proportionately much greater; the availability of the nitrogen to crops is increased by this raising of the nitrogen-carbon ratio. Much useful information, on the agricultural use of sewage sludges and of straw-sludge compost, submitted in a style which the

<sup>58</sup> *Proc. Amer. Soc. Civil Eng.*, 1945, **71**, 307; B., 1945, III, 134.

<sup>59</sup> *Ibid.*, 1944, **70**, 1276; B., 1945, III, 133.

<sup>60</sup> *Nature*, 1943, **152**, 249; B., 1944, III, 268.

<sup>61</sup> *J. Inst. Sewage Purif.*, 1944, 46; B., 1946, III, 167.



ordinary farmer can understand, is provided in a memorandum published by the Agricultural Research Council.<sup>62</sup>

A. H. Niles<sup>63</sup> has made a very useful contribution to the literature of the subject, with special reference to the dried sludge produced at Toledo, Ohio. He reports that results have demonstrated that the value of the product is far greater than would be expected from its ordinary nitrogen-phosphate-potash assessment. In this connexion, he draws attention to the nitrogen-fixing organisms in sewage sludge, and to the presence of many valuable elements the presence of which is essential to plant metabolism. This is not the only recent opinion to the effect that sewage sludge may be beneficial in hitherto unappreciated directions. Until fairly recently it seemed to be fairly commonly accepted that sewage sludge was useful only as a source of nitrogen and humus. More recent investigations have shown that the sludge can supply, amongst other things, very useful amounts of available phosphate. Interesting particulars of the phosphate contents of twelve types of sewage sludge were provided by W. Rudolfs and H. W. Gehm<sup>64</sup> two or three years ago. The total phosphate content (as  $P_2O_5$ ) of these sludges varied from 1.49 to 4.6%; the insoluble phosphate ranged from 0.22 to 0.61%, and the available phosphate for 1.19 to 4.23%. Of course, it has long been known that sludge contained appreciable quantities of phosphate; the notable development has been the demonstration that much of this phosphate is readily utilised by plants.

### *Rural Sewage Disposal.*

The official policy—and it is a sound policy—of taking piped water supplies to rural communities is bound to give rise to problems of sewage disposal, and it is wise that attention should be given to this matter in time to prevent the fouling of streams. Some of the problems which may arise have been considered by G. T. Cotterell,<sup>65</sup> who drew attention to the general difficulties which may sometimes occur through abnormal proportions of farm drainage or milk wastes in the sewage.

After surveying the present position in rural sewerage and sewage disposal, N. C. Little<sup>66</sup> discussed future prospects. He noted the fact that in some instances the smallness (in all respects) of the sewerage system might give rise to special difficulties, as variations in the nature and volume of the sewage would be transmitted—with little opportunity for “averaging”—direct to the purification plant; also in such small sewerage systems there would be little time for the disintegration of coarse solids, or for the cooling of discharges of hot liquids. Discussing methods of treatment, the author expressed the opinion that sedimentation

<sup>62</sup> *J. Inst. Sewage Purif.*, 1944, 59; B., 1946, III, 168.

<sup>63</sup> *Sewage Works J.*, 1944, 16, 720; B., 1944, III, 268.

<sup>64</sup> *New Jersey Agric. Exp. Sta.*, 1942, *Bull.* 699; B., 1945, III, 83.

<sup>65</sup> *J. Roy. San. Inst.*, 1944, 64, 19.

<sup>66</sup> *Surveyor*, 1945, 104, 225.



followed by biological filtration is preferable to such methods as the old septic tank. He also emphasised the desirability, whenever practicable, of taking the sewage from a group of hamlets to a single treatment plant. His views on these matters are undoubtedly sound. The case for making full use of modern plants such as filters equipped with revolving distributors is equally strong. Less advanced designs such as septic tanks and beds equipped with fixed (and woefully inefficient) distributors are often preferred on the grounds that they require less attention. This is often an erroneous assumption. It is true that such plants usually receive little attention but this is often due to neglect rather than to the fact that they do not need regular maintenance. To give equal performance many such plants need far more attention than do works equipped with modern apparatus specially designed to suit the requirements of small installations.

### *Sewage Analysis.*

As the determination of chloride in sewage is a routine test and as the usual silver nitrate method is subject to interference by various substances frequently occurring in sewages containing industrial wastes, the method suggested by O. Sturz<sup>67</sup> is of considerable interest. It is claimed to eliminate the effect of most of the complicating substances, and to be both rapid and accurate. The chloride is titrated in dilute nitric acid with mercuric nitrate, using diphenylcarbazone as indicator in the presence of ether, which sharpens the end-point by intensifying the red colour of the mercury-diphenylcarbazone complex. Oxalic acid and hydrogen peroxide are used to prevent interference.

W. D. Hatfield and G. E. Symons<sup>68</sup> have contributed some notes on the determination of grease in sewage. In the recommended method the sample is acidified with concentrated hydrochloric acid to a pH of 1.0, boiled for 2 minutes, cooled, and kept in a refrigerator for at least 2 hours. This is followed by filtration through a cotton disc on a 9-cm. paper; the latter is dried at 103° for 30—40 minutes, and extracted in a Soxhlet apparatus with light petroleum for 3—5 hours. Any emulsified grease not removed by chilling and filtration is extracted by light petroleum and added to the main portion, but this is reported to be unnecessary with liquid sludges.

A disadvantage of the standard methylene-blue method of determining the relative stability of sewage effluents is the long period of incubation needed to obtain results. S. H. Hopper and O. W. Briscoc<sup>69</sup> have carried out some work aimed at obtaining reliable indications in a shorter time. In their experiments they explored the possibility of using several other dyes (covering a wide range of redox potential) in place of methylene-blue. They also used a special sodium thioglycollate medium to facilitate

<sup>67</sup> *Chem.-Ztg.*, 1943, **67**, 57; C., 1945, III, 52.

<sup>68</sup> *Sewage Works J.*, 1945, **17**, 16; C., 1945, III, 191.

<sup>69</sup> *Ibid.*, 1944, **16**, 558; C., 1945, III, 52.



the growth of anaërobes, and tested the effect of incubation at 37° instead of 20°. They report that by using brilliant-cresyl-blue with sodium thioglycollate medium and incubating at 20°, relative stability can be determined in about one fifth of the time required by the standard methylene-blue method.

### *Biology of Sewage Disposal.*

L. A. Allen<sup>70</sup> has made a valuable addition to our knowledge of the bacteriology of activated sludge. Preliminary experiments disclosed that homogenisation of the sludge, to disrupt the flocs, increased the number of culturable organisms by ten to one hundred times. Later experiments investigated the predominant flora of activated sludge obtained from a sewage works and of an activated sludge produced in the laboratory, while his paper also contains an interesting account of the bacteriological changes occurring during the aëration process. In a few lines it is useless to attempt a summary of this paper, which merits study in its unabridged form.

The same worker, in collaboration with T. G. Tomlinson and I. L. Norton,<sup>71</sup> has carried out a research on the effect of treatment in percolating filters on bacterial counts. Amongst other matters, the paper traces seasonal variations in the bacterial content of effluents from percolating filters, and compares the bacterial quality of effluents from alternating double filtration and conventional filtration processes respectively. The ordinary single filter effected much the greater removal of bacteria, achieving a reduction of well over 90% on the feed liquor under favourable circumstances.

Mention must be made of a very thorough consideration by H. Wilson<sup>72</sup> of some of the risks of transmission of disease during the treatment, disposal, and utilisation of sewage, sewage effluent, and sewage sludge. Although possibly written with an eye mainly to South African conditions, it contains much interesting information of general applicability. It would appear that if reasonable precautions are taken, none of the operations covered by the paper need offer any serious menace to health. No doubt the object of the author was to draw attention to these "reasonable precautions."

### *Trade Effluents.*

With changes in industrial processes, and the obligation of local authorities to take liquid trade wastes into public sewers, the properties and purification of trade effluents have become matters of paramount importance. For this reason, the mass of recent literature on the subject will no doubt receive thorough consideration. There is certainly plenty of material for study; so much so, that it will only be possible here to give brief mention to certain of the more important contributions.

<sup>70</sup> *J. Hygiene*, 1944, 43, 426; B., 1945, III, 179.

<sup>71</sup> *J. Inst. Sewage Purif.*, 1944, 115; B., 1946, III, 186.

<sup>72</sup> *Ibid.*, 214; B., 1946, III, 186.



Some of the publications concerning waste liquors from the metal trades deserve the careful attention of sewage technicians, for they indicate methods of removing at the source certain constituents which are particularly dangerous to sewers and sewage purification. N. Swindin<sup>73</sup> has collected a lot of valuable information on the recovery of acid from pickling liquors, giving details of methods which have proved satisfactory at recent British plants. He makes the interesting suggestion that ferrous sulphate should be collected from pickling plants for roasting at a central depot; the recovered acid would be returned to the pickling plants. The recovery of dichromate and sulphuric acid from waste chrome liquors was the subject of a publication by G. C. Mitter and S. G. Dighe,<sup>74</sup> who recounted their experiences with an electrolytic process. F. S. Friel and G. J. Wiest<sup>75</sup> have submitted some notes on the removal of cyanide from metal finishing wastes; after chemical precipitation of other toxic substances, cyanides were converted into innocuous ammonium carbonate by chlorination.

During the war the disposal of waste liquors from the preparation of vegetables for drying gave rise to many difficulties. Potato wastes were particularly troublesome, one reason being their tendency to rapid putrefaction, a fact which made long-period sedimentation undesirable. The position was made more difficult by the fact that such factories were often located in rural areas, where public sewage disposal works were either non-existent or of small size. E. E. Jones<sup>76</sup> has reported that a detention period of two hours is satisfactory in horizontal-flow tanks, and that when treated on biological filters (either alone or in admixture with domestic sewage) the settled wastes represented a load roughly equivalent to that of an equal volume of domestic sewage of equivalent strength. Considering the difficult nature of the waste liquors produced, it is perhaps fortunate that the dehydration of vegetables is not likely to be carried out on such a large scale in peace-time.

A. C. Barnes<sup>77</sup> has summarised various methods for the disposal of sugar-factory and distillery wastes. It seems that there is room for further work in this field, for none of the methods for disposing of these troublesome wastes appears to be particularly convenient.

The treatment and disposal of waste waters from paper mills has been dealt with by B. A. Southgate.<sup>78</sup> In his opinion, fully satisfactory methods for use in paper mills which produce pulp by the caustic soda process have not yet been found. He feels that the most hopeful line of attack is to improve the efficiency of caustic soda recovery, and to treat the resultant liquor by coagulation and sedimentation, followed by biological

<sup>73</sup> *Chem. Trade J.*, 1944, **114**, 465.

<sup>74</sup> *J. Sci. Ind. Res., India*, 1943, **2**, 11; B., 1944, I, 233.

<sup>75</sup> *Water Works and Sewerage*, 1945, **92**, 97; B., 1945, III, 156.

<sup>76</sup> *J.S.C.I.*, 1945, **64**, 80; B., 1945, III, 156.

<sup>77</sup> *J.A.S.T. Quart.*, 7, No. 1, 8; B., 1945, III, 83.

<sup>78</sup> *Paper Maker*, 1945, **109**, TS 43; **110**, TS 1; B., 1945, III, 180.



purification. T. E. Brookover<sup>79</sup> has provided some useful data on the coagulation and clarification stages of paper waste treatment.

Viscose-rayon manufacturing wastes are very complex, and in the past their treatment has presented serious difficulties. For this reason, a very capable discussion on the subject by E. T. Roetman<sup>80</sup> is of special interest. He has described the manufacturing process, given particulars of the waste liquors produced at each stage, and detailed methods for their treatment, both alone and in admixture with domestic sewage. His account of the American work on this subject is very impressive, but the results achieved by some British rayon factories, working in collaboration with municipal sewage undertakings, have nothing to fear from comparison.

The treatment of some chemical industry wastes at a large American factory has been described by T. Powers.<sup>81</sup> The liquors consist of phenolic and general chemical wastes. The treatment is comprehensive, comprising a storage pond, a Dorr clarifier, percolating filters, activated-sludge units, and finally, effluent ponds. The overall removal of phenol is of the order of 94—99%.

H. W. Gehm<sup>82</sup> has gone thoroughly into the question of the treatment of laundry wastes. Amongst a mass of valuable data there is the interesting information that the use of 100 p.p.m. of magnesium sulphate and 1000 p.p.m. of lime, with a mixed commercial laundry waste, give complete clarification, 90% removal of B.O.D., and a sludge which compacted well. The dosages of chemicals are high, but the results obtained are striking.

The broad aspects of industrial waste disposal have been thoughtfully considered by G. E. Symons.<sup>83</sup> Although he was mainly concerned with American conditions, his article is of wider appeal as an aid to getting the subject into true perspective.

#### RIVER POLLUTION PREVENTION.

There have recently been some very interesting contributions on the pollution potential of various types of trade wastes. For example, L. Newton<sup>84</sup> has dealt with the pollution of the rivers of West Wales by lead- and zinc-mine effluent. He found that lack of vegetation and paucity of fish life were due mainly to the presence of zinc and some lead, derived from galena and blende from old mine dumps. Deficiency of phosphate was a secondary cause of poor vegetation. He reported that this type of mining pollution cannot be entirely prevented by the provision of silt pits, but filtration through peat was effective. B. G.

<sup>79</sup> *Paper Trade J.*, 1945, 120, *TAPPI Sect.*, 95; B., 1945, III, 135.

<sup>80</sup> *Water Works and Sewerage*, 1944, 91, 265, 295; B., 1945, III, 31.

<sup>81</sup> *Sewage Works J.*, 1945, 17, 330; B., 1945, III, 180.

<sup>82</sup> *Ibid.*, 1944, 16, 571; B., 1944, III, 268.

<sup>83</sup> *Ibid.*, 1945, 17, 538; B., 1945, III, 200.

<sup>84</sup> *Ann. Appl. Biol.*, 1944, 31, 1; B., 1945, III, 31.



Anderson<sup>85</sup> has described a method of using daphnids as test animals for detecting toxic materials in trade wastes and waters. The article includes a table showing the threshold concentrations for the immobilisation of daphnids by 42 substances when added to centrifuged Lake Erie water.

A paper by M. M. Ellis<sup>86</sup> on the effect of industrial wastes on fish life is both informative and easy to read. He summarises the ways, in addition to direct poisoning, in which fish may be killed by industrial wastes, and gives convincing instances to emphasise his points. Then there is his reminder that fish are unable to take average samples—they have to live for the moment, and once dead they have no further interest in stream conditions. The point that conditions which damage any link in the long chain of aquatic life may eventually prove fatal to the whole system is also worth remembering.

H. Clay<sup>87</sup> has provided a useful summary of some problems connected with river pollution, including some notes on criteria for sewage effluents, coupled with a reminder of standards of river quality which these criteria presuppose and are intended to maintain.

<sup>85</sup> *Sewage Works J.*, 1944, **16**, 1156; B., 1945, III, 116.

<sup>86</sup> *Water Works and Sewerage*, 1945, **92**, 171.

<sup>87</sup> *J. Inst. Sewage Purif.*, 1944, 109; B., 1946, III, 187.



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